Gold(III) Salen Complex-Catalyzed Synthesis of Propargylamines via a Three-Component Coupling Reaction

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Supporting Information

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General Procedure for Synthesis of Gold(III) Salen Complexes 1a-e

To a suspension of $KAuCl_4$ (0.2 mmol) in CH_2Cl_2 (10 mL) was added a solution of NH_4PF_6 (1.3 mmol) in EtOH (10 mL). After dropwise addition of a solution of salen ligand (1 mmol) in CH_2Cl_2 (10 mL), the reaction mixture was refluxed for 20 min. After cooling, diethyl ether or hexane was added to the reaction mixture to induce precipitation. The precipitate was collected and washed with chloroform. The solid collected was then dissolved in CH_3CN and filtered. The filtrate was concentrated under reduced pressure to give gold(III) salen complexes **1a-e**.

General Procedure for Gold(III) Salen Complex-Catalyzed Three-Component Coupling Reaction

A mixture of **1a** (0.02 mmol), aldehyde (2.0 mmol), amine (2.2 mmol) and alkyne (3.0 mmol) in water (1 mL) were stirred at 40 ^oC for 24 h in the absence of light under N_2 atmosphere. The reaction mixture was extracted with diethyl ether (3×15 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The product was purified by flash column chromatography on silica gel using ethyl acetate-hexane as eluent.

General Procedure for Synthesis of Artemisinin Derivatives 5-7

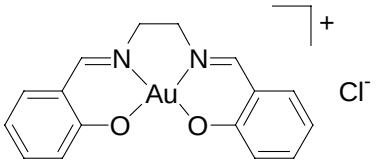
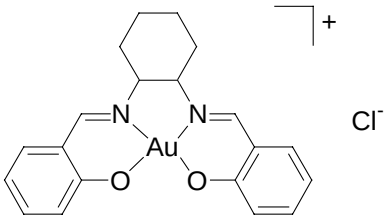
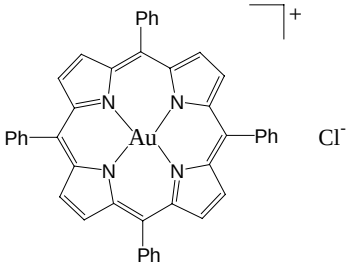
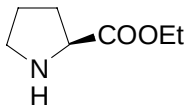
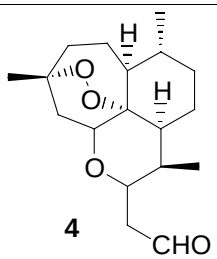
A mixture of **1a** (0.005 mmol), aldehyde **4** (0.1 mmol), amine (0.22 mmol) and alkyne (0.3 mmol) in water (1 mL) were stirred at 40 ^oC for 24 h in the absence of light under N_2 atmosphere. The reaction mixture was extracted with diethyl ether (3×15 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The product was purified by flash column chromatography on silica gel using ethyl acetate-hexane as eluent.

Cytotoxicity Studies (MTT Assay)

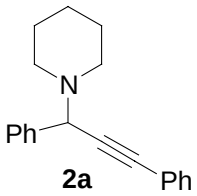
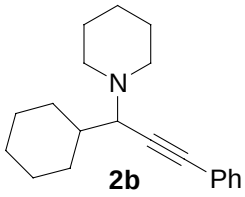
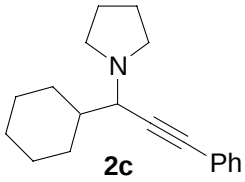
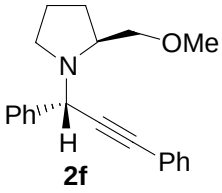
Human hepatocellular carcinoma (HepG2) was maintained in a minimum essential medium with Earle's balanced salts (MEM). All the media were supplemented with 2 mM *L*-glutamine and 10% fetal boviene serum. Penicillin (100 U/mL) and Streptomycin (100 μg/mL) were added to all media. Cultures were incubated at 37 °C in a 5% CO_2/ 95% air humidified atmosphere.

Assays on the cytotoxic effects were conducted in 96-well flat-bottomed microtitre plates. The supplemented culture medium (100 μL) with cells (4×10^4 cells/ mL) was added into each well and was incubated (37 °C, 5% CO_2/ 95% air) for 24 h. All the media were then removed and fresh supplemented medium (100 μL) was added into each well. Compounds **5-7** dissolved in the culture medium (100 μL + < 1 % ethanol) were added into a set of wells. After mixing, the sample-containing media (100 μL) were drawn and added to another set of wells. Such processes were repeated to provide a set of two-fold dilution series. Controlled wells only contained 100 μL of supplemented media. Microtitre plates were incubated at 37 °C in a 5% CO_2/ 95% air humidified atmosphere for further 6 days. All the cytotoxicity assays were run in parallel with a negative control (i.e., untreated population). Assessment of the cytotoxicity was carried out using a modified method of Mosmann based 3-(4, 5-Dimethylthiazol-2-yl)-2, 5-diphenyltetrazolium bromide (MTT) Assay [Mosmann, T. *J. Immunol. Methods* **1983**, 65, 55 – 63.]. At the end of each incubation period, 10 μL of the MTT solution (Cell Proliferation Kit I, Roche) were added into each well and the cultures were further incubated for 4 h at 37 ^{o}C in a 5% CO_2/ 95% air humidified atmosphere. Then 100 μL of the solubilization solution was added into the wells to lyse the cells and solubilize the formazan complex formed. The microtitre plates were maintained in a dark and humidified chamber overnight. The formation of formazan was measured with a microtitre plate reader at 550 nm, and the percentages of cell survival were determined. The cytotoxicity was evaluated based on the percentage cell survival in a dose-dependence manner relative to the negative control.

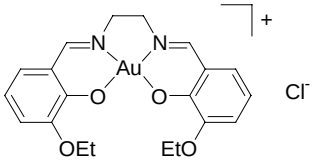
Literature References of 1a, 1c, [Au(TPP)Cl], (S)-Ethyl Prolinoate and Artemisinin Aldehyde 4

 **1a**	a) Barnholtz, S. L. et. al., *Inorg. Chem.* **2001**, *40*, 972. b) Sun, R. W. Y. et. al., *ChemBioChem.* **2004**, *5*, 1293.
 **1c**	Banerjee, K. et. al., *Indian J. of Chem, Section A* **1984**, *23A*, 555.
 [Au(TPP)Cl]	a) Sun, R. W. Y. et. al., *Chem. Commun.* **2003**, 1718. b) Sun, R. W. Y. et. al., *ChemBioChem.* **2004**, *5*, 1293.
 (S)-Ethyl Prolinoate	Federsel, H. J. et. al., *J. Org. Chem.* **1990**, *55*, 2254.
 **4**	Liu, L. et. al., *Org. Lett.* **2005**, *7*, 1561.

Literature References of Propargylamines 2a-c, 2f

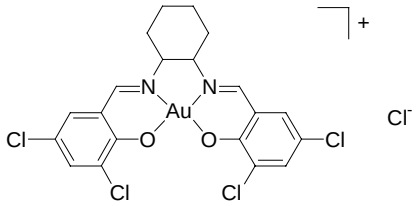
 **2a**	a) Wei, C. et. al., *J. Am. Chem. Soc.* **2003**, *125*, 9584. b) Wei. C. et. al., *Org. Lett.* **2003**, *5*, 4473. c) Shi, L. et. al., *Org. Lett.* **2004**, *6*, 1001.
 **2b**	a) Wei, C. et. al., *Org. Lett.* **2003**, *5*, 4473. b) Li, Z., et. al., *Tetrahedron Lett.* **2004**, *45*, 2443.
 **2c**	Wei, C. et. al., *Org. Lett.* **2003**, *5*, 4473.
 **2f**	Gommermann, N. et. al., *Angew. Chem. Int. Ed.* **2003**, *42*, 5763.

Characterization Data of Gold(III) Salen Complex 1b, 1d-e



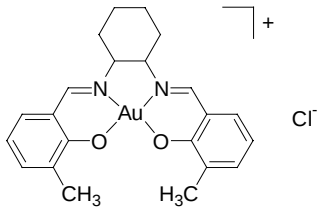
1b

Brownish yellow solid; ^{1}H NMR (300 MHz, CD_3CN) δ 8.45 (s, 2H), 6.99-6.92 (m, 4H), 6.79-6.71(t, J = 7.9 Hz, 2H), 4.10-4.03 (q, J = 7.0 Hz, 4H), 3.93 (s, 4H), 1.41-1.36 (t, J = 7.0 Hz, 6H); IR (KBr, cm^{-1}) 1633, 1496, 1454; FAB-MS *m/z* 551 (M^+).



1d

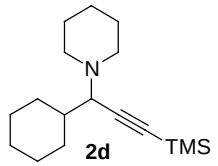
Orange solid; ^{1}H NMR (300 MHz, CD_3CN) δ 8.35 (s, 2H), 7.94-7.93 (d, *J* = 2.6 Hz, 2H), 7.81-7.80 (d, *J* = 2.6 Hz, 2H), 4.07-4.05 (m, 2H), 2.83-2.79 (m, 2H), 1.88-1.86 (m, 2H), 1.60-1.45 (m, 2H); IR (KBr, cm^{-1}) 1628, 1593, 1435, 1321; FAB-MS *m/z* 655 (M^+).



1e

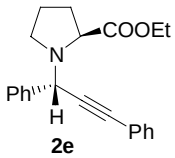
Orange solid, ^{1}H NMR (300 MHz, CD_3CN) δ 8.36 (s, 2H), 7.65-7.62 (m, 4H), 6.97-6.92 (t, *J* = 7.5 Hz, 2H), 3.99-3.96 (m, 2H), 2.84-2.80 (d, *J* = 11.7 Hz, 2H), 2.38 (s, 6H), 1.90-1.80 (m, 2H), 1.53-1.47 (t, *J* = 9.9 Hz, 2H); IR (KBr, cm^{-1}) 1602, 1552, 1313; FAB-MS *m/z* 545 (M^+).

Characterization Data of Propargylamines 2d – 2e, 2g – 2i



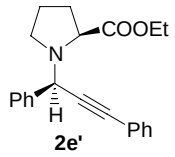
2d

Colorless oil; analytical TLC (silica gel 60) (10% EtOAc in hexane), R_f = 0.51; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.89-2.86 (d, *J* = 10.0 Hz, 1H), 2.55-2.47 (m, 2H), 2.30-2.26 (m, 2H), 2.03-1.94 (m, 2H), 1.75-1.39 (m, 11H), 1.23-1.14 (m, 2H), 1.00-0.84 (m, 2H), 0.18 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 104.12, 89.77, 64.59, 50.55, 39.30, 31.15, 30.37, 29.72, 26.82, 26.27, 26.24, 26.10, 24.74, 0.42; IR (KBr, neat, cm^{-1}) 2158; EIMS *m/z* 277 (M^+); HRMS (EI) for $C_{17}H_{31}NSi$, calcd 277.2226, found 277.2221.



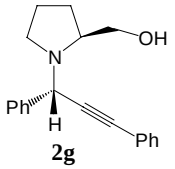
2e

Yellow oil; analytical TLC (silica gel 60) (10% EtOAc in hexane), R_f = 0.29; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70-7.68 (d, *J* = 7.4 Hz, 2H), 7.53-7.50 (m, 2H), 7.38-7.25 (m, 6H), 5.27 (s, 1H), 4.32-4.18 (m, 2H), 3.78-3.73 (dd, *J* = 9.0, 6.9 Hz, 1H), 2.79-2.66 (m, 2H), 2.25-1.99 (m, 2H), 1.82-1.74 (m, 2H), 1.34-1.29 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.10, 139.11, 131.88, 128.36, 128.32, 128.29, 128.24, 127.59, 123.06, 87.98, 85.32, 63.25, 60.72, 57.30, 47.37, 29.33, 23.24, 14.37; IR (KBr, neat, cm^{-1}) 2361, 1741; EIMS *m/z* 333 (M^+); HRMS (EI) for $C_{22}H_{23}NO_2$, calcd 333.1729, found 333.1742.



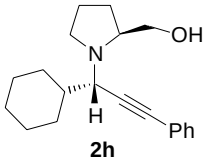
2e'

Yellow oil; analytical TLC (silica gel 60) (10% EtOAc in hexane), R_f = 0.15; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60-7.58 (d, *J* = 7.2 Hz, 2H), 7.51-7.48 (m, 2H), 7.35-7.27 (m, 6H), 5.12 (s, 1H), 3.82-3.74 (q, *J* = 7.1 Hz, 2H), 3.61-3.57 (dd, *J* = 9.3, 4.5 Hz, 1H), 3.34-3.30 (td, *J* = 8.4, 2.7 Hz, 1H), 3.04-2.96 (m, 1H), 2.16-1.91 (m, 2H), 1.89-1.83 (m, 2H), 1.05-1.01 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.75, 138.14, 131.86, 128.87, 128.44, 128.36, 128.35, 128.31, 128.28, 128.14, 127.88, 122.98, 87.12, 86.37, 60.85, 60.31, 58.54, 53.03, 30.89, 29.71, 24.07, 14.12; IR (KBr, neat, cm^{-1}) 2361, 1741; EIMS *m/z* 333 (M^+); HRMS (EI) for $C_{22}H_{23}NO_2$, calcd 333.1729, found 333.1742.



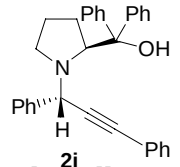
2g

Pale yellow oil; analytical TLC (silica gel 60) (30% EtOAc in hexane), R_f = 0.24; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61-7.59 (d, *J* = 7.2 Hz, 2H), 7.53-7.48 (m, 2H), 7.40-7.30 (m, 6H), 5.12 (s, 1H), 3.86-3.81 (dd, *J* = 10.9, 3.5 Hz, 1H), 3.56-3.51 (dd, *J* = 10.9, 2.2 Hz, 1H), 3.31-3.27 (m, 1H), 2.86-2.77 (dd, *J* = 9.2, 7.3 Hz, 1H), 2.66-2.59 (td, *J* = 8.0, 3.0 Hz, 1H), 1.97-1.92 (m, 1H), 1.87-1.75 (m, 1H), 1.73-1.66 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.18, 131.85, 128.46, 128.40, 128.37, 128.34, 128.31, 128.09, 127.62, 122.99, 87.83, 85.37, 61.83, 61.75, 56.25, 47.90, 28.04, 23.60; IR (KBr, neat, cm^{-1}) 3436, 2361, 2341; EIMS m/z 291 (M^+); HRMS (EI) for $C_{20}H_{21}NO$, calcd 291.1623, found 291.1617.



2h

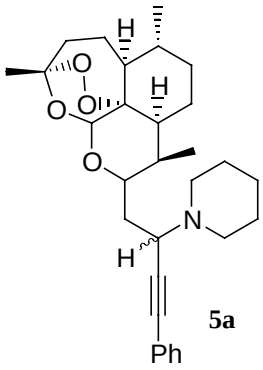
Yellow oil; analytical TLC (silica gel 60) (30% EtOAc in hexane), R_f = 0.56; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.40 (m, 2H), 7.30-7.28 (m, 3H), 3.68-3.63 (dd, *J* = 10.9, 3.4 Hz, 1H), 3.42-3.38 (dd, *J* = 10.8, 3.0 Hz, 2H), 3.13-3.08 (m, 1H), 2.91-2.81 (m, 2H), 2.16-2.05 (m, 2H), 1.92-1.51 (m, 8H), 1.36-1.87 (m, 4H), 1.08-0.87 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 131.74, 128.09, 127.95, 123.33, 87.23, 86.00, 61.97, 61.26, 56.59, 47.18, 41.21, 31.43, 30.29, 27.78, 26.60, 26.08, 25.94, 23.98; IR (KBr, neat, cm^{-1}) 3449, 2361; EIMS *m/z* 266 (M^+-CH_2OH); HRMS (EI) for $C_{19}H_{24}N$, calcd 266.1909, found 266.1908.



2i

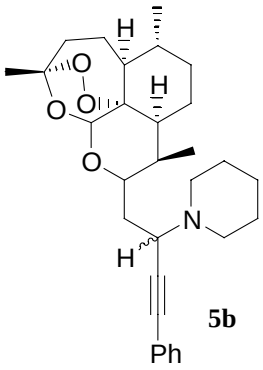
Pale yellow oil; analytical TLC (silica gel 60) (10% EtOAc in hexane), R_f = 0.39; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86-7.83 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.64-7.61 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.57-7.54 (m, 2H), 7.40-7.37 (m, 3H), 7.32-7.29 (m, 6H), 7.26-7.21 (m, 3H), 7.20-7.12 (m, 2H), 4.69 (s, 1H), 4.52-4.49 (q, *J* = 5.0 Hz, 1H), 4.27 (s, 1H), 2.98-2.89 (td, *J* = 9.1, 7.1 Hz, 1H), 1.98-1.82 (m, 1H), 1.81-1.60 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.98, 146.53, 139.19, 131.89, 128.74, 128.43, 128.40, 128.32, 128.12, 128.11, 127.99, 127.90, 127.44, 127.02, 126.68, 126.28, 125.49, 125.46, 123.16, 87.58, 85.83, 77.89, 68.10, 57.90, 49.48. 30.92, 29.89, 24.26; IR (KBr, neat, cm^{-1}) 3391, 2360; FAB-MS *m/z* 444 (M^++H)

Characterization Data of Artemisinin Derivatives 5–7



5a

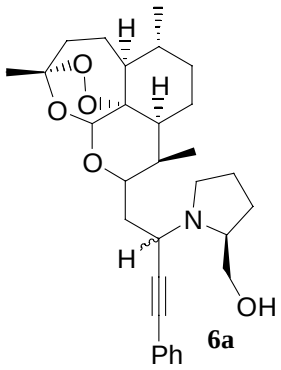
Pale yellow oil; analytical TLC (silica gel 60) (40% EtOAc in hexane), R_f = 0.34; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44-7.41 (m, 2H), 7.32-7.28 (m, 3H), 5.23 (s, 1H), 4.04-3.99 (dd, *J* = 10.9, 3.8 Hz, 1H), 3.71-3.63 (td, *J* = 10.1, 2.1 Hz, 1H), 2.71-2.64 (m, 2H), 2.59-2.56 (m, 2H), 2.37-2.30 (m, 2H), 2.03-1.92 (m, 2H), 1.89-1.84 (m, 2H), 1.69-1.20 (m, 13H), 1.40 (s, 3H), 0.95-0.93 (d, *J* = 6.2 Hz, 3H), 0.83-0.81 (d, *J* = 7.1 Hz, 3H), 1.09-0.85 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 131.76, 128.22, 127.76, 123.72, 103.99, 92.11, 88.09, 85.92, 80.78, 71.85, 54.84, 52.07, 50.73, 46.36, 37.32, 37.10, 36.42, 34.22, 32.32, 30.36, 29.71, 26.20, 26.01, 24.81, 24.56, 21.48, 20.33, 14.10; IR (KBr, neat, cm^{-1}) 2361; EIMS *m/z* 479 (M^+); HRMS (EI) for $C_{30}H_{41}NO_4$, calcd 479.3036, found 479.3046.



5b

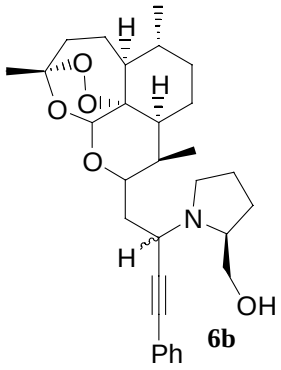
Pale yellow oil; analytical TLC (silica gel 60) (40 % EA in hexane), R_f = 0.48; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44-7.41 (m, 2H), 7.28-7.26 (m, 3H), 5.24 (s, 1H), 3.97-3.92 (dd, *J* = 9.3, 5.0 Hz, 1H), 3.76-3.69 (td, J = 10.1, 2.1 Hz, 1H), 2.62-2.58 (m, 2H), 2.48-2.35 (m, 4H), 2.06-1.98 (m, 2H), 1.90-1.71 (m, 2H), 1.69-1.08 (m, 13H), 1.41 (s, 3H), 0.97-0.95 (d, *J* = 6.3 Hz, 3H), 0.84-0.81 (d, *J* = 7.1

Hz, 3H), 1.07-0.88 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 131.71, 128.16, 127.62, 103.94, 92.11, 80.92, 70.95, 53.68, 52.09, 50.32, 46.41, 37.35, 36.43, 34.27, 36.43, 34.27, 31.93, 31.76, 30.33, 29.94, 29.71, 29.37, 26.30, 26.15, 24.83, 24.67, 22.70, 21.45, 20.34, 14.12, 14.04; IR (KBr, neat, cm^{-1}) 2360; EIMS *m/z* 479 (M^+); HRMS (EI) for $C_{30}H_{41}NO_4$, calcd 479.3036, found 479.3056.



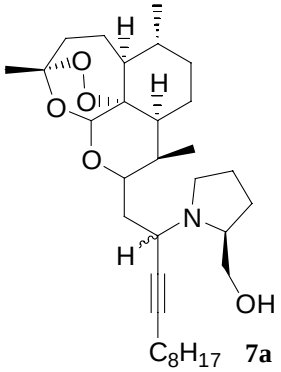
6a

Pale yellow oil; analytical TLC (silica gel 60) (50 % EA in hexane), R_f = 0.32; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.39 (m, 2H), 7.30-7.28 (m, 3H), 5.23 (s, 1H), 4.36-4.33 (dd, *J* = 10.6, 5.0 Hz, 1H), 3.69-3.63 (td, *J* = 11.0, 3.4 Hz, 2H), 3.39-3.35 (dd, *J* = 11.0, 5.3 Hz, 1H), 3.14-3.08 (m, 1H), 2.94-2.84 (m, 2H), 2.38-2.26 (m, 3H), 2.03-1.73 (m, 6H), 1.72-1.61 (m, 3H), 1.55-1.51 (m, 2H), 1.49-1.44 (m, 1H), 1.42 (s, 3H), 1.40-1.32 (m, 1H), 1.27-1.21 (m, 2H), 1.04-0.97 (m, 1H), 0.95-0.94 (d, *J* = 6.3 Hz, 3H), 0.83-0.81 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 131.71, 128.22, 127.82, 123.43, 104.14, 92.21, 88.65, 84.61, 80.84, 70.30, 64.36, 62.14, 52.04, 48.99, 47.27, 46.17, 37.81, 37.22, 36.29, 34.17, 32.46, 27.72, 26.04, 24.67, 24.24, 21.54, 20.30, 13.75; IR (KBr, neat, cm^{-1}) 3468, 2361, 2341, 2245, 1641; EIMS *m/z* 495 (M^+); HRMS (EI) for $C_{30}H_{41}NO_5$, calcd 495.2985, found 495.2990.



6b

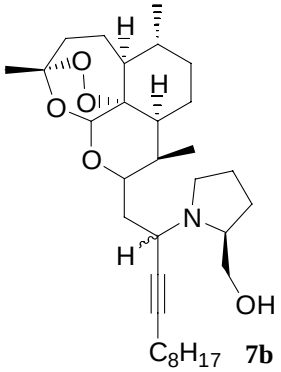
Pale yellow oil; analytical TLC (silica gel 60) (50 % EA in hexane), R_f = 0.05; ^{1}H NMR (300MHz, $CDCl_3$) δ 7.42-7.39 (m, 2H), 7.32-7.29 (m, 3H), 4.24-4.19 (m, 1H), 3.72-3.63 (m, 1H), 3.58-3.53 (dd, *J* = 10.4, 4.36 Hz, 1H), 3.40-3.29 (m, 2H), 3.19-3.13 (m, 1H), 2.96-2.88 (m, 1H), 2.42-2.27 (m, 2H), 2.04-1.21 (m, 18H), 1.42 (s, 3H), 0.96-0.94 (d, *J* = 6.18Hz, 3H), 0.83-0.81 (d, *J* = 7.16 Hz, 3H), 1.07-0.86 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 131.71, 128.31, 127.97, 123.45, 104.08, 92.27, 89.27, 80.88, 77.46, 72.02, 65.38, 59.73, 54.16, 52.52, 52.11, 46.29, 38.76, 37.35, 36.41, 34.20, 32.46, 30.12, 29.72, 26.07, 24.77, 21.55, 20.33, 14.07; IR (KBr, neat, cm^{-1}) 3437, 2360, 2341; EIMS *m/z* 464 (M-CH_2OH).



7a

Colorless oil; analytical TLC (silica gel 60) (50 % EA in hexane), R_f = 0.40; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.20 (s, 1H), 4.10-4.05 (m, 1H), 3.64-3.56 (m, 2H), 3.34-3.30 (dd, *J* = 10.9, 5.1 Hz, 1H), 3.03-2.97 (m, 1H), 2.82-2.74 (m, 2H), 2.37-2.26 (m, 2H), 2.20-2.16 (td, *J* = 6.9, 1.9 Hz, 2H), 2.02-1.96 (m, 1H), 1.87-1.55 (m, 1H), 1.52-1.45 (m, 10H), 1.44 (s, 3H), 1.38-1.32 (m, 2H), 1.28-1.18 (m, 11H), 1.06-0.99 (td, *J* = 12.5, 3.3 Hz, 1H), 0.94-0.93 (d, *J* = 6.3 Hz, 3H), 0.90-0.87 (t, *J* = 6.9 Hz,

3H), 0.79-0.78 (d, J = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 104.08, 92.17, 84.52, 80.85, 78.55, 70.34, 64.15, 61.88, 52.07, 48.37, 46.93, 46.21, 38.16, 37.21, 36.31, 34.20, 32.42, 31.84, 29.24, 29.13, 29.10, 28.81, 27.72, 26.04, 24.67, 24.16, 22.66, 21.54, 20.29, 18.63, 14.10, 13.74; IR (KBr, neat, cm^{-1}) 3452, 2361, 1641; EIMS *m/z* 500 (M^+ - CH_2OH); HRMS (EI) for $C_{31}H_{49}NO_4$, calcd 500.3740, found 500.3752.



7b

Colorless oil; analytical TLC (silica gel 60) (50 % EA in hexane) R_f = 0.10; ^{1}H NMR δ 5.20 (s, 1H), 3.98-3.93 (m, 1H), 3.64-3.57 (td, J = 9.7, 2.3 Hz, 1H), 3.54-3.49 (m, 1H), 3.36-3.31 (dd, J = 10.5, 3.5 Hz, 1H), 2.23-3.19 (m, 1H), 3.08-3.04 (m, 1H), 2.86-2.77 (m, 2H), 2.31-2.25 (m, 2H), 2.22-2.17 (m, 2H), 2.05-1.67 (m, 10H), 1.50-1.47 (m, 4H), 1.46 (s, 3H), 1.33-1.21 (m, 10H), 1.09-1.00 (m, 1H), 0.96-0.94 (d, J = 6.2 Hz, 3H), 0.90-0.86 (t, J = 6.5 Hz, 3H), 0.80-0.78 (d, J = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 103.99, 92.21, 84.77, 80.87, 72.00, 65.34, 59.34, 52.08, 46.28, 38.75, 37.36, 36.38, 34.21, 32.34, 31.93, 30.20, 29.70, 29.25, 29.11, 28.86, 26.06, 24.69, 22.69, 21.54, 22.69, 21.54, 20.33, 18.70, 14.11; IR (KBr, neat, cm^{-1}) 3439, 2352; EIMS *m/z* 531 (M^+).

^{1}H NMR Spectra of Diastereomeric Mixtures of 2e-g, 2i

Table 2, entry 5

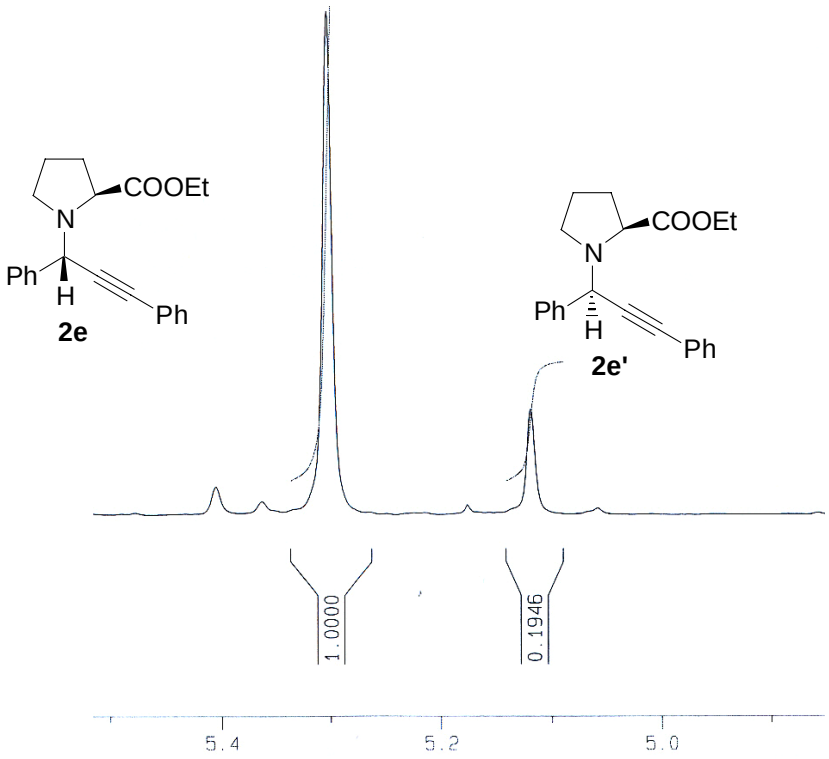


Table 2, entry 6

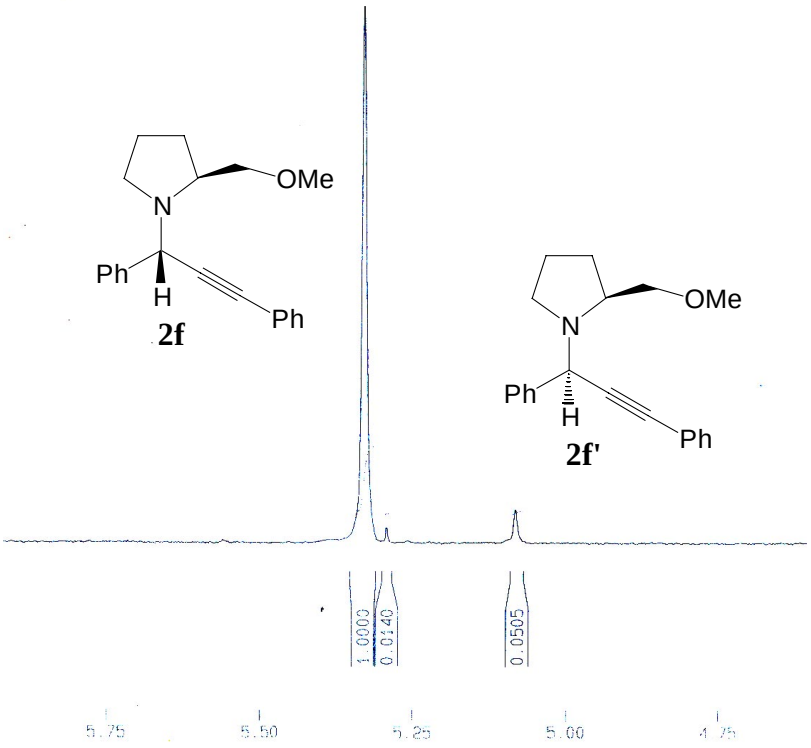


Table 2, entry 7

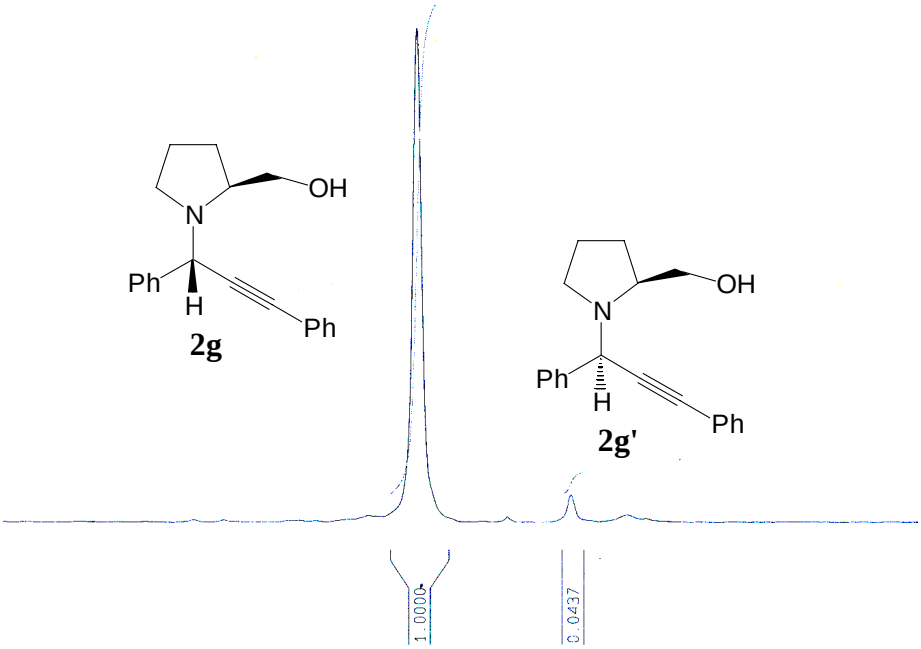
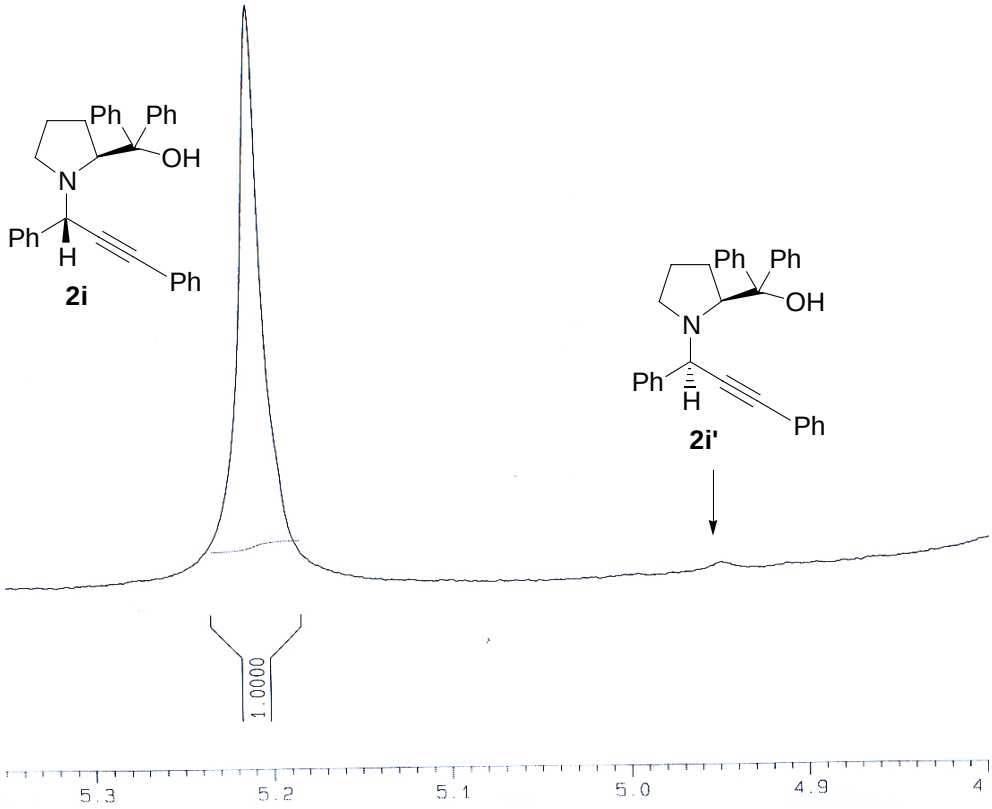
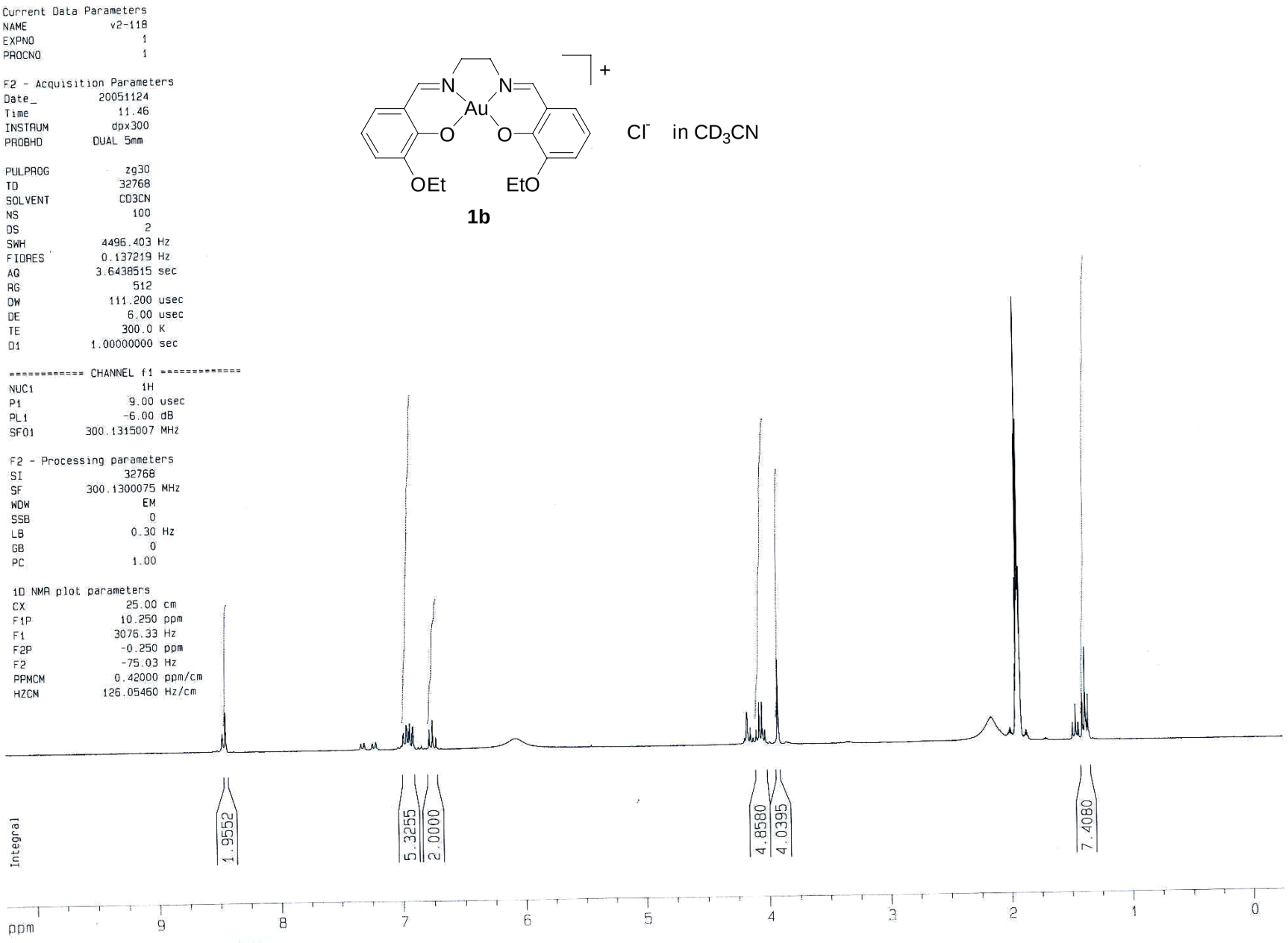


Table 2, entry 9

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SWH 4496.403 Hz
FIDRES 0.137219 Hz
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RG 512
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DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
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PL1 -6.00 dB
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F2 - Processing parameters
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SF 300.1300075 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
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F1 3076.33 Hz
F2P -0.250 ppm
F2 -75.03 Hz
PPMCM 0.42000 ppm/cm
HZCM 126.05460 Hz/cm
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N
Au
O
O
OEt
EtO
+
Cl-
in CD3CN
1b
Integral
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7
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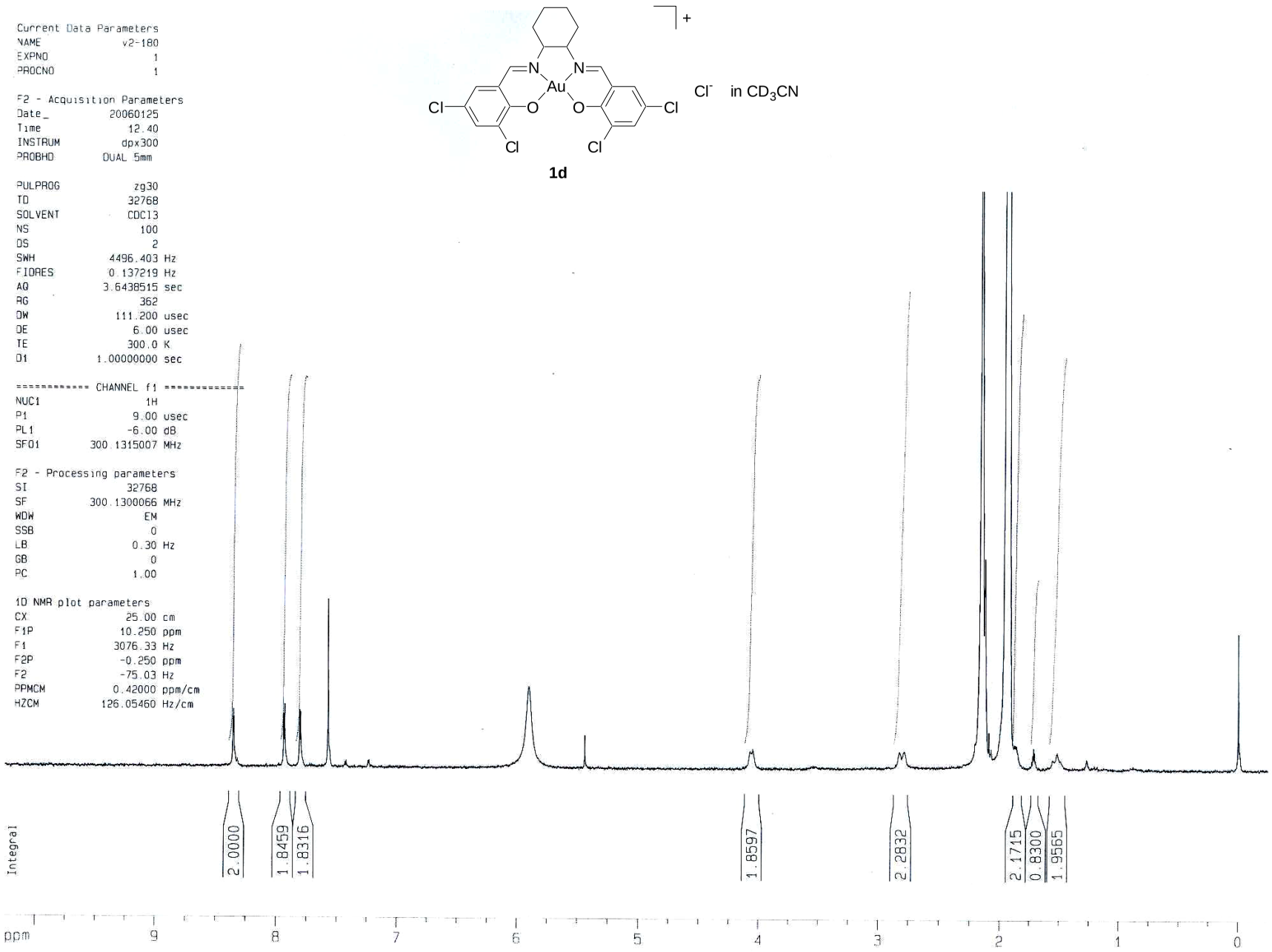
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PROCNO 1
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TD 32768
SOLVENT CDCl3
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DS 2
SWH 4496.403 Hz
FIDRES 0.137219 Hz
AQ 3.6438515 sec
RG 362
DW 111.200 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
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P1 9.00 usec
PL1 -6.00 dB
SFO1 300.1315007 MHz
F2 - Processing parameters
SI 32768
SF 300.1300066 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 25.00 cm
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F1 3076.33 Hz
F2P -0.250 ppm
F2 -75.03 Hz
PPMCM 0.42000 ppm/cm
HZCM 126.05460 Hz/cm
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Au
O
Cl⁻ in CD3CN
1d
Integral
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7
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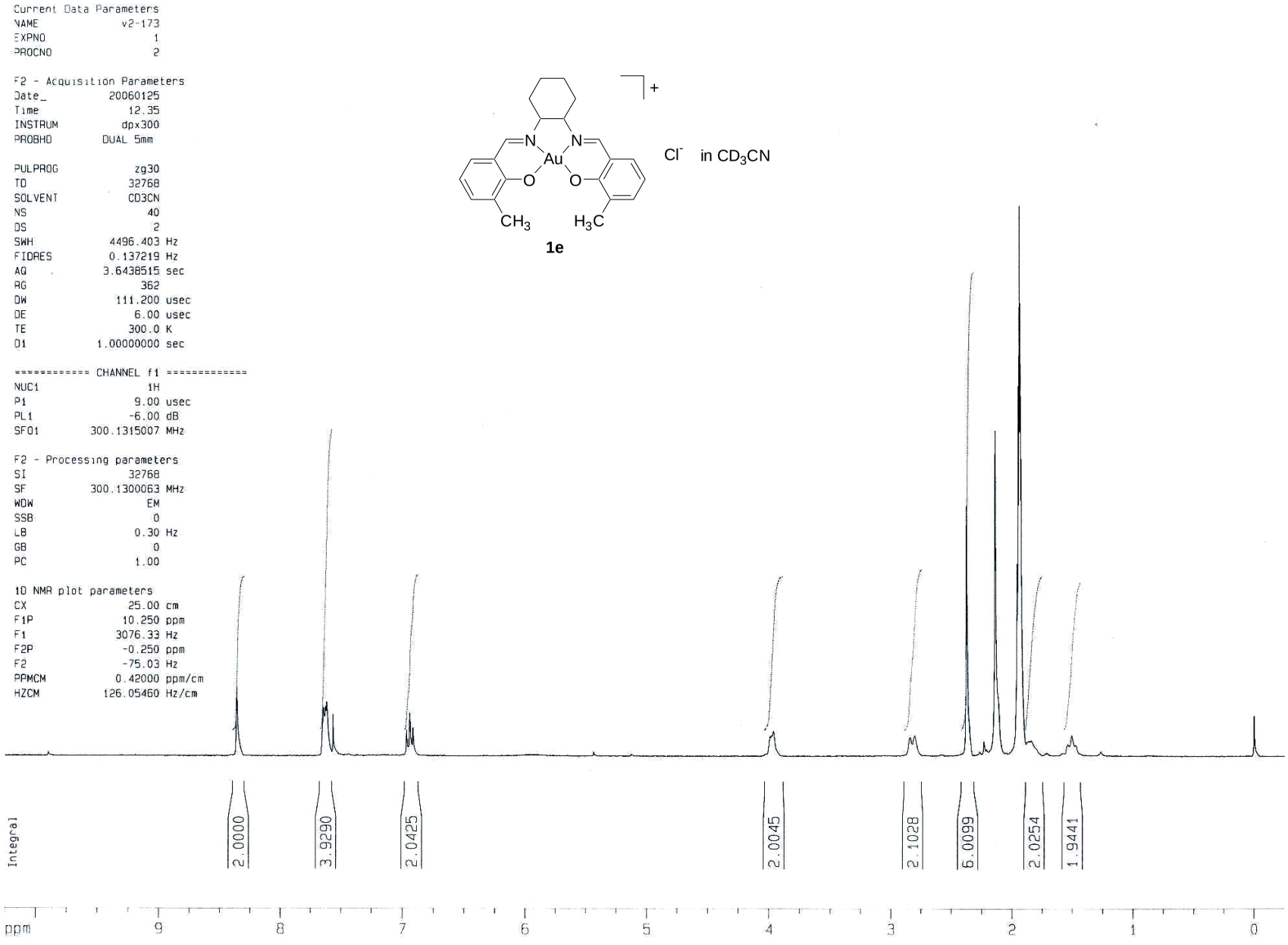
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TD 32768
SOLVENT CD3CN
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DS 2
SWH 4496.403 Hz
FIDRES 0.137219 Hz
AQ 3.6438515 sec
RG 362
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DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
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P1 9.00 usec
PL1 -6.00 dB
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SF 300.1300063 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
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F1P 10.250 ppm
F1 3076.33 Hz
F2P -0.250 ppm
F2 -75.03 Hz
PPMCM 0.42000 ppm/cm
HZCM 126.05460 Hz/cm
N
Au
N
O
O
CH3
H3C
+
Cl- in CD3CN
1e
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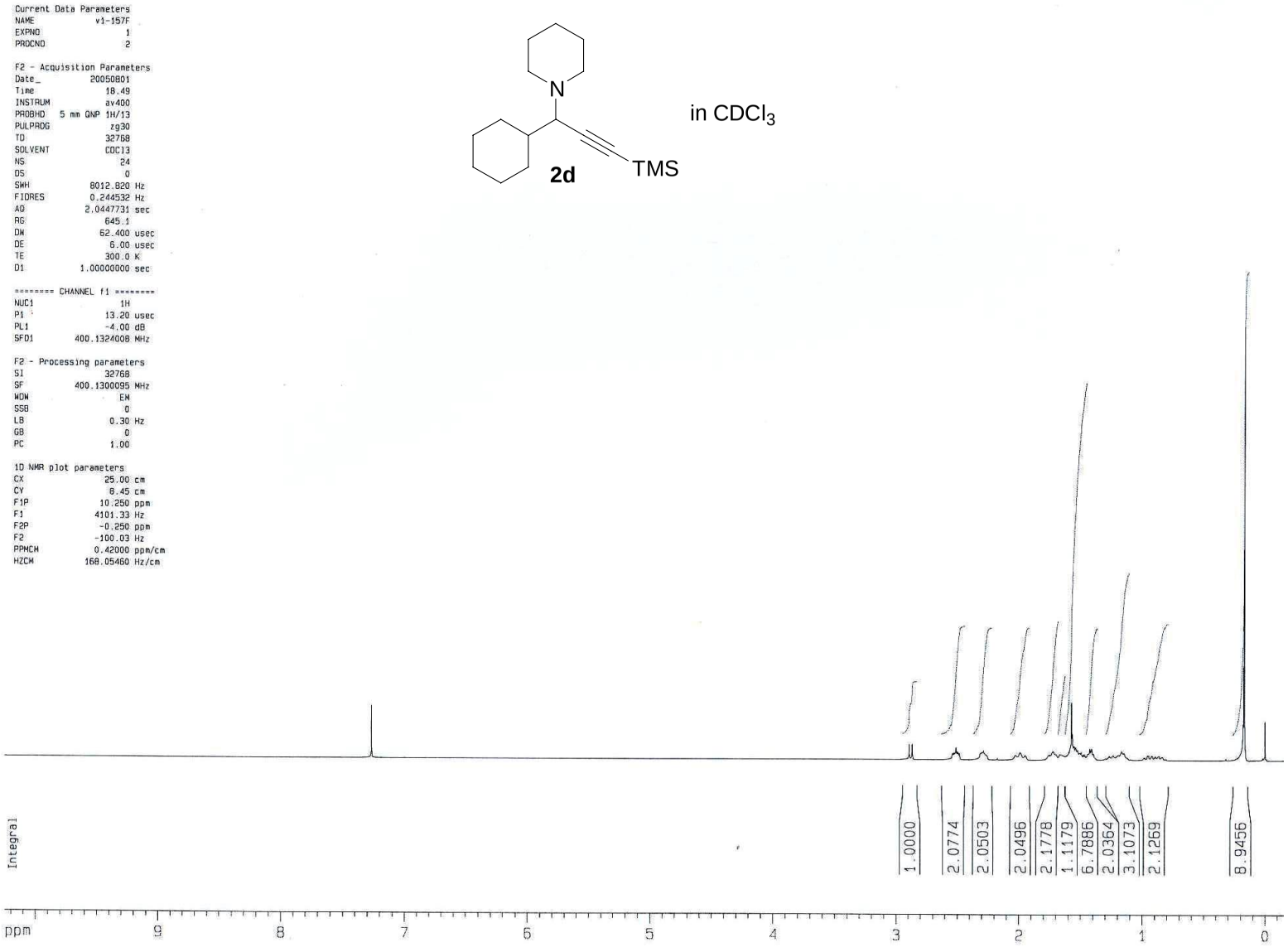
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SOLVENT CDCl3
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FIDRES 0.244532 Hz
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RG 645.1
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DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
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PL1 -4.00 dB
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N
TMS
2d
in CDCl3
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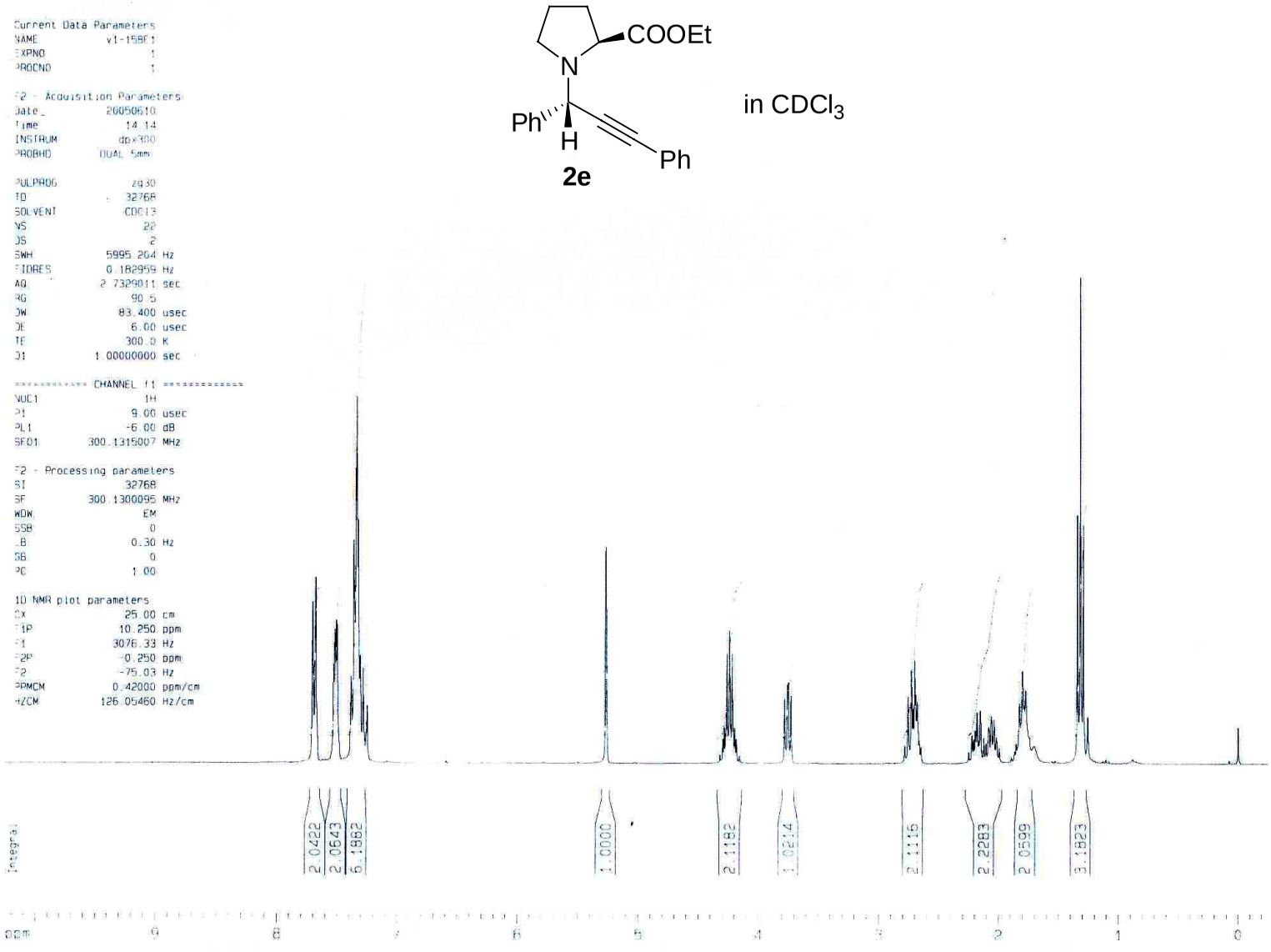
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FIDRES 0.182959 Hz
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DE 6.00 usec
TE 300.0 K
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PL1 -6.00 dB
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F2 - Processing parameters
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SF 300.1300095 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 25.00 cm
F1P 10.250 ppm
F1 3076.33 Hz
F2P -0.250 ppm
F2 -75.03 Hz
PPMCM 0.42000 ppm/cm
HZCM 126.05460 Hz/cm
COOEt
N
Ph
H
Ph
2e
in CDCl3
Integral
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ppm
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7
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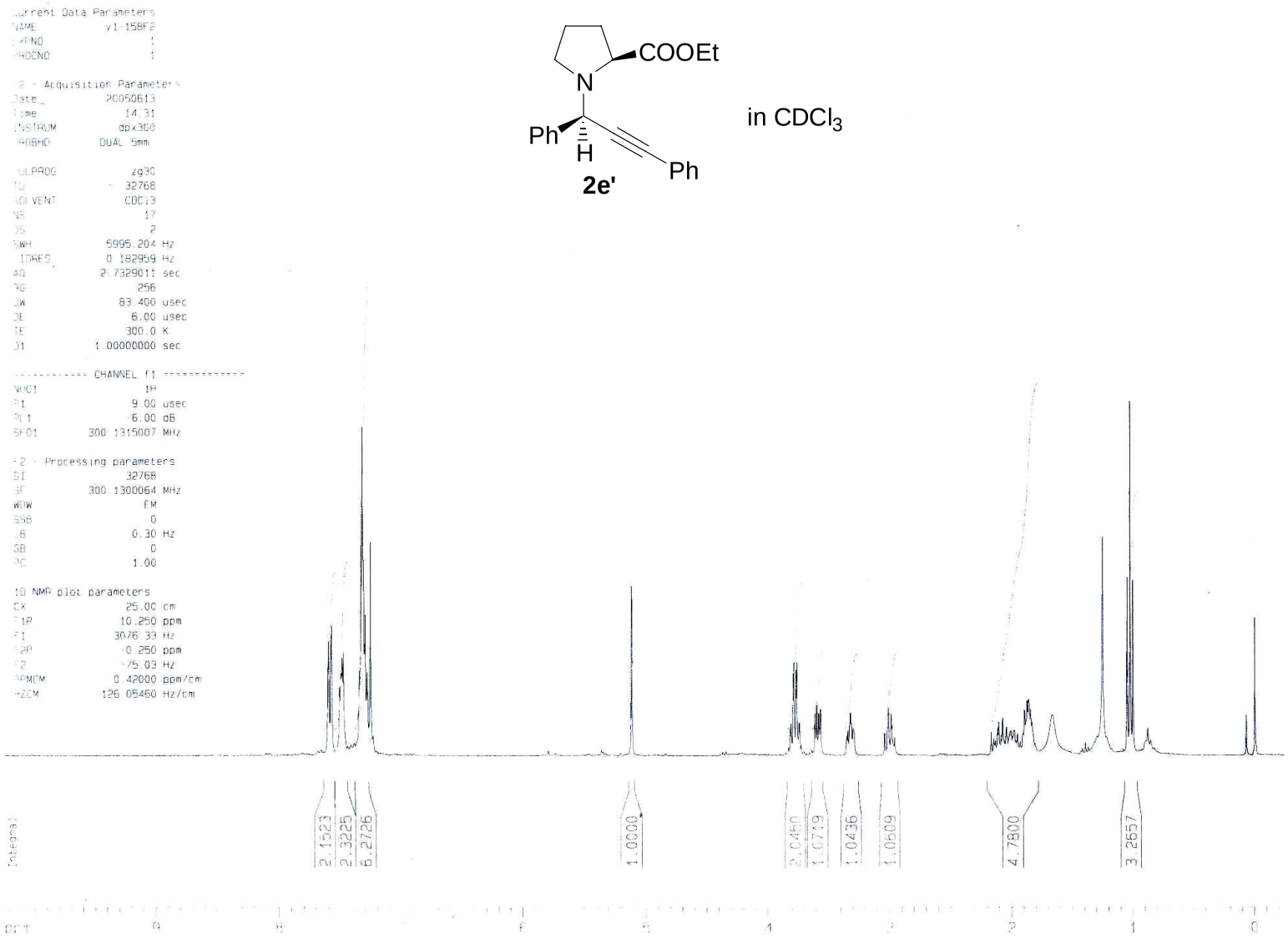
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NUC1 1H
P1 9.00 usec
PL1 6.00 dB
SFO1 300.1315007 MHz
F2 - Processing parameters
SI 32768
SF 300.1300064 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 25.00 cm
F1P 10.250 ppm
F1 3076.33 Hz
F2P -0.250 ppm
F2 -75.03 Hz
PPMCM 0.42000 ppm/cm
HZCM 126.05460 Hz/cm
COOEt
N
Ph
H
Ph
2e'
in CDCl3
Integral
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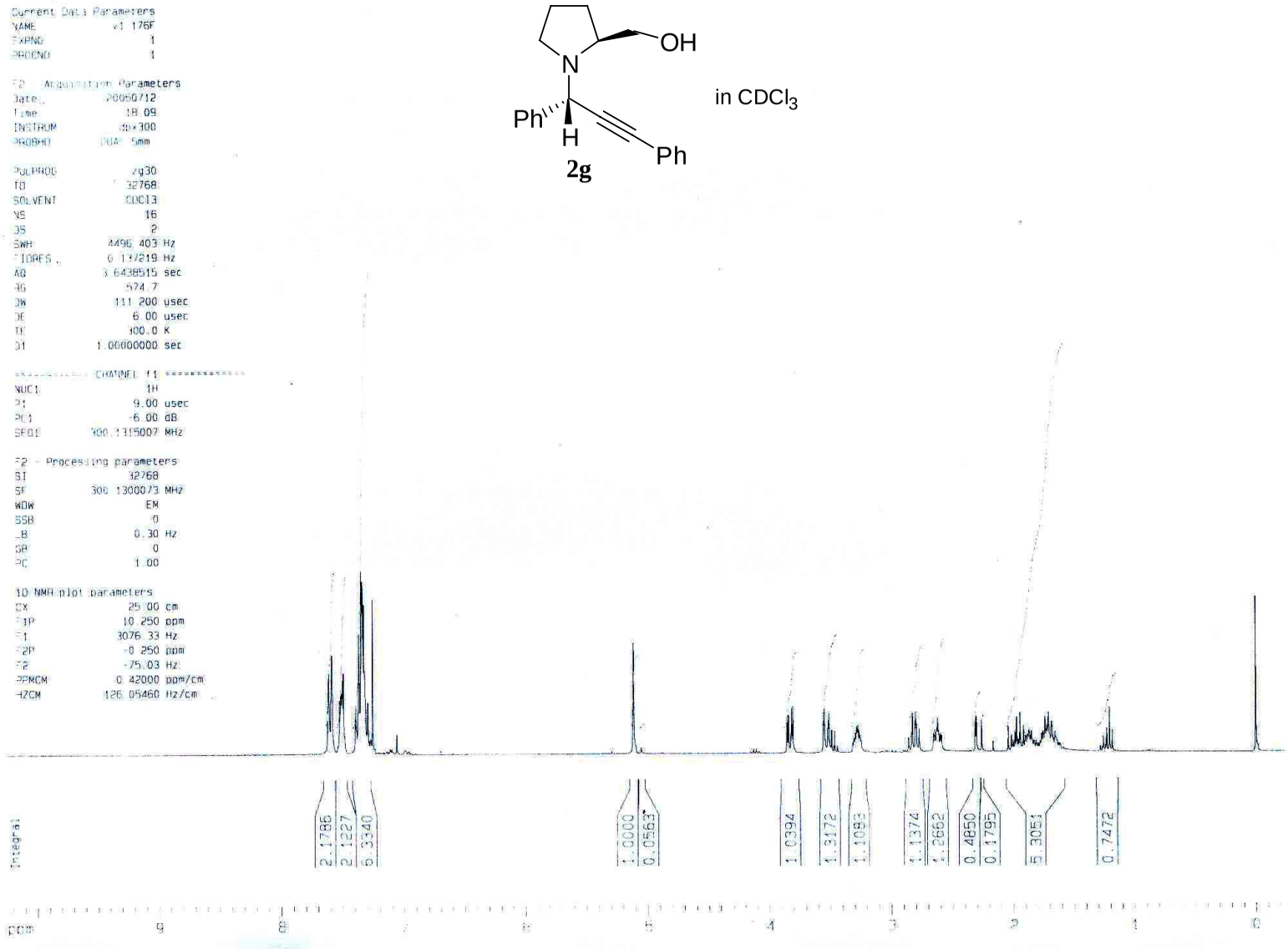
ppm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TD 32768
SOLVENT CDCl3
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SWH 4496.403 Hz
FIDRES 0.137219 Hz
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RG 574.7
DW 111.200 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
CHANNEL f1
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P1 9.00 usec
PL1 -6.00 dB
SFO1 300.1315007 MHz
F2 - Processing parameters
SI 32768
SF 300.1300073 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 25.00 cm
F1P 10.250 ppm
F1 3076.33 Hz
F2P -0.250 ppm
F2 -75.03 Hz
PPMCM 0.42000 ppm/cm
HZCM 126.05460 Hz/cm
OH
N
Ph
H
Ph
2g
in CDCl3
Integral
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1.1083
1.1374
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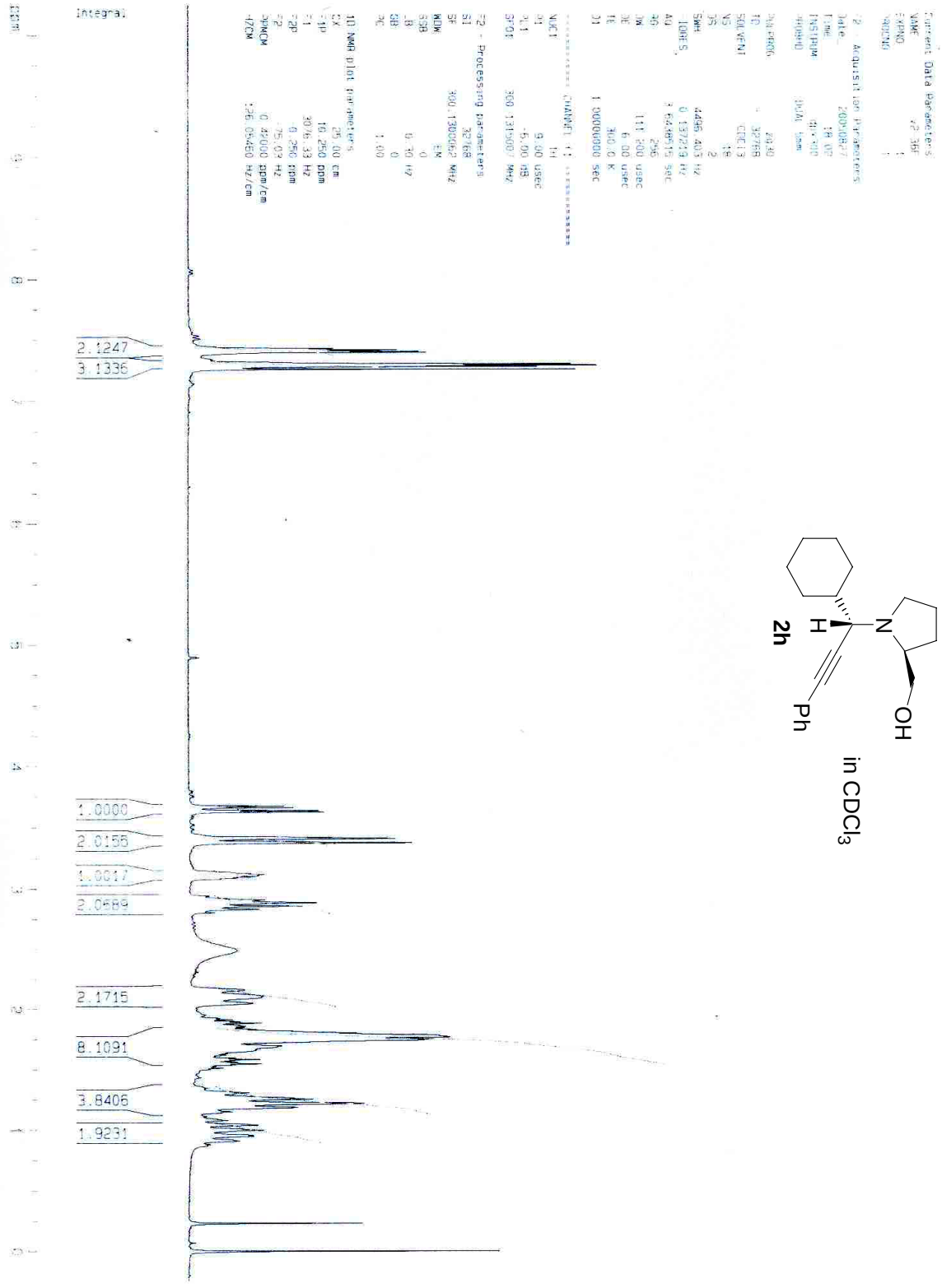
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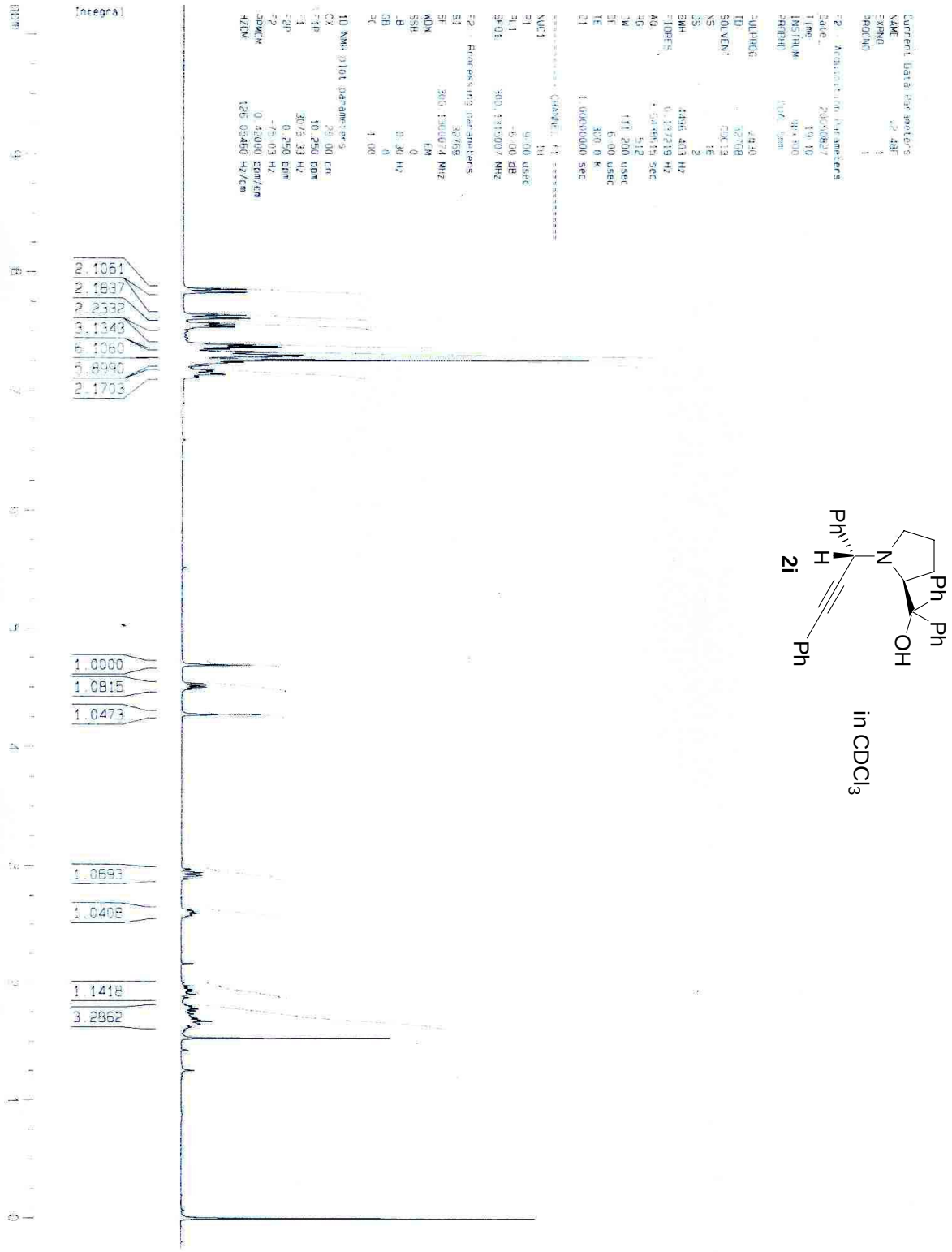
in CDCl3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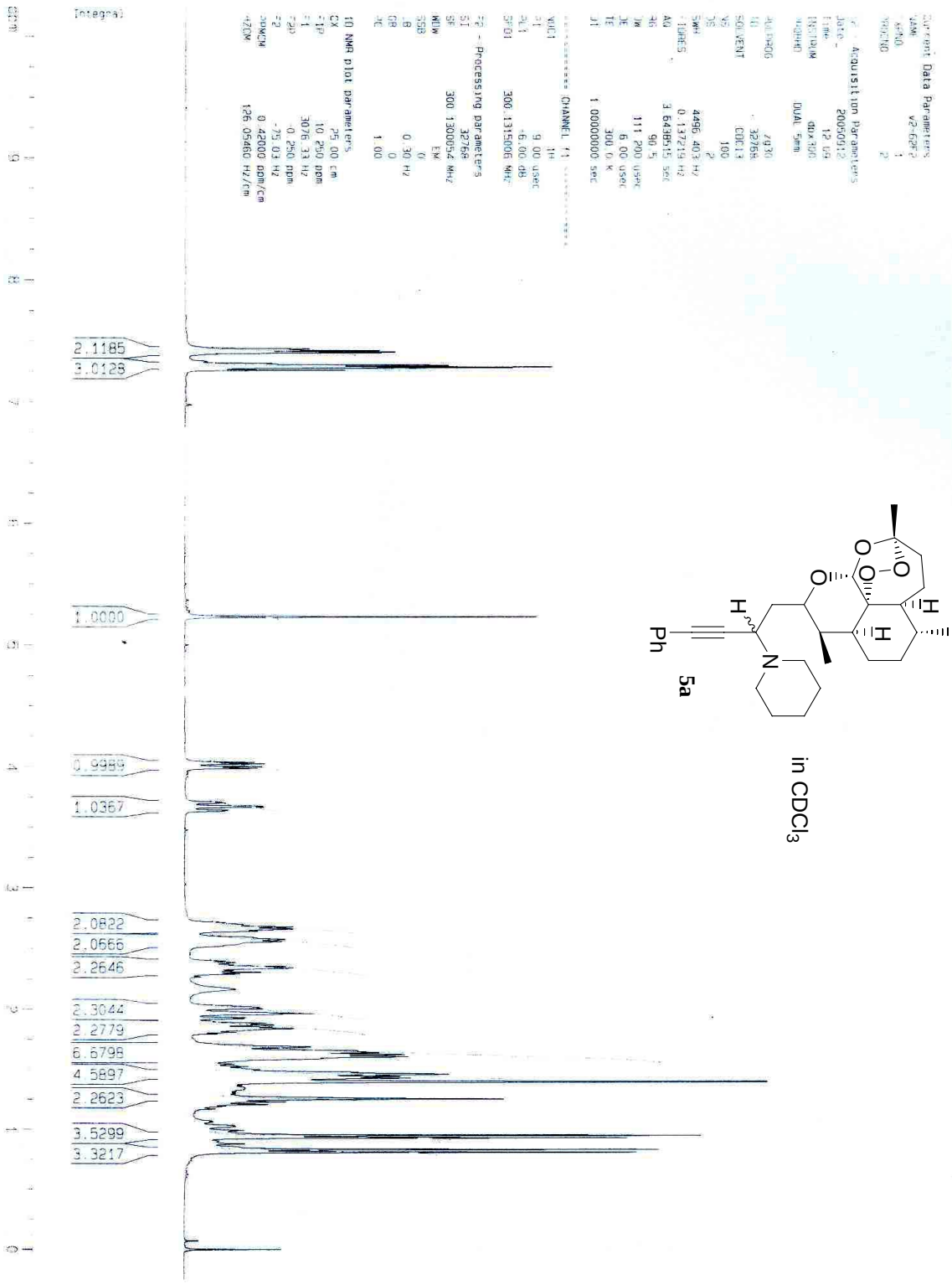
in CDCl3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O
O
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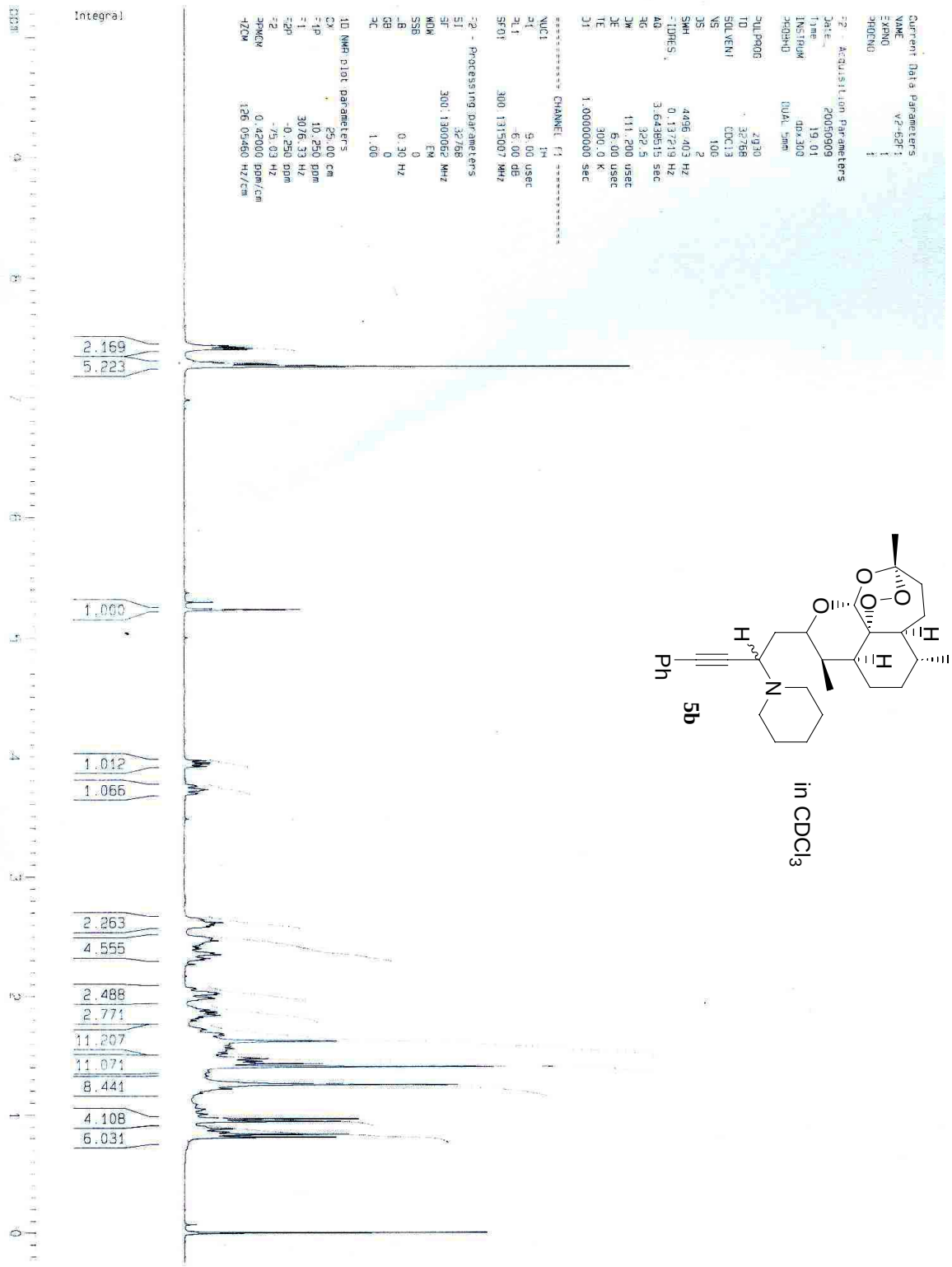
N
5a
in CDCl3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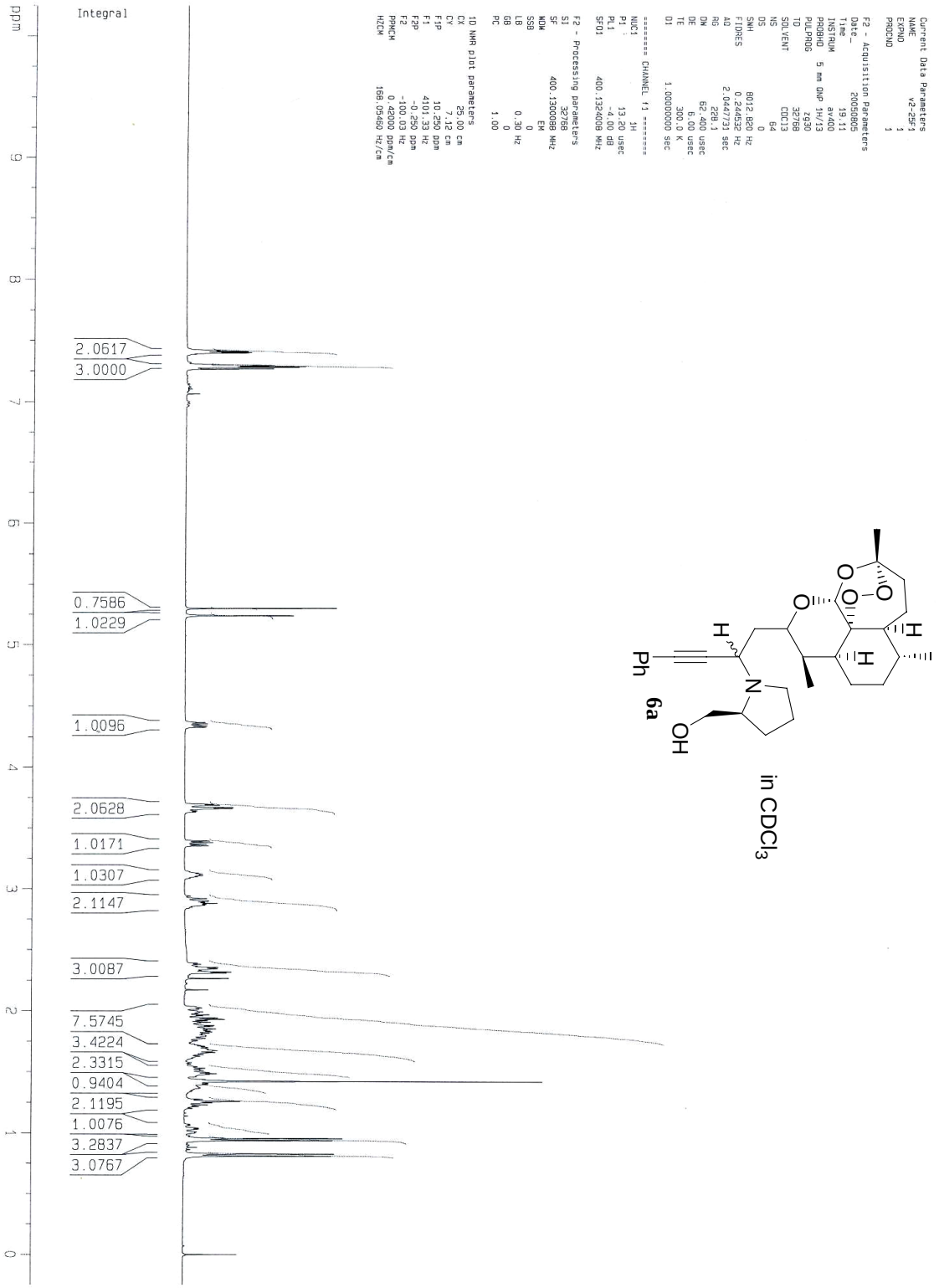
in CDCl3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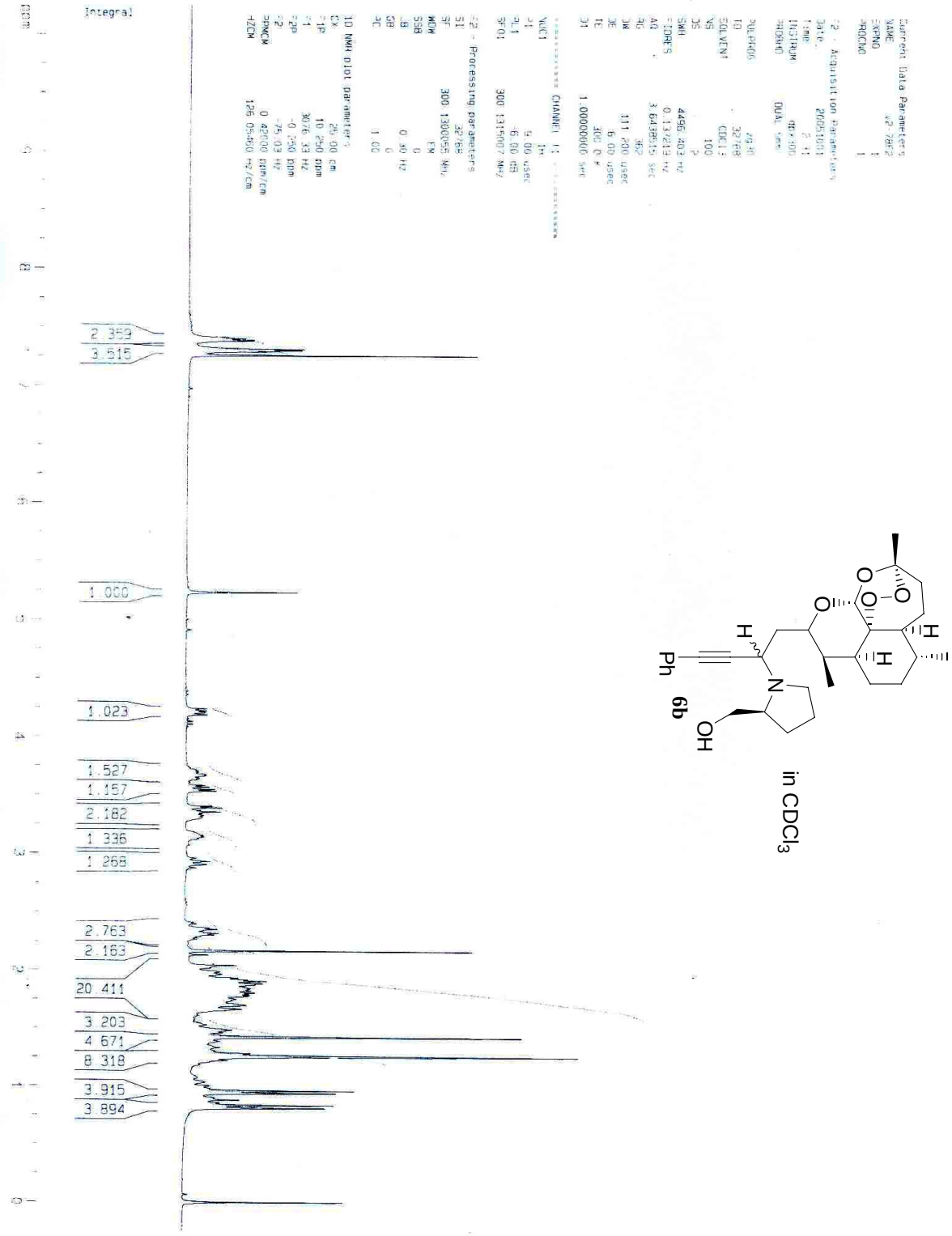
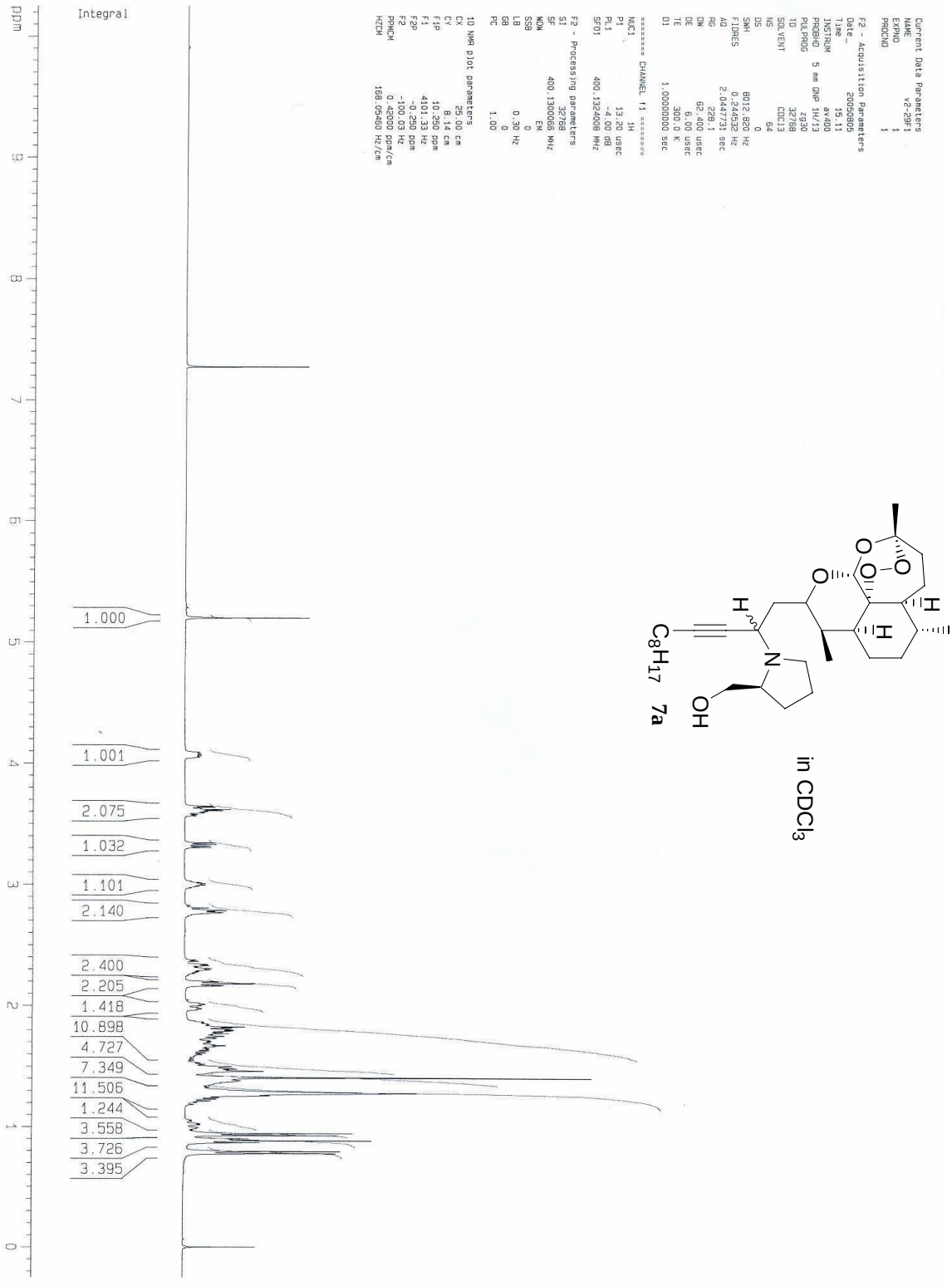
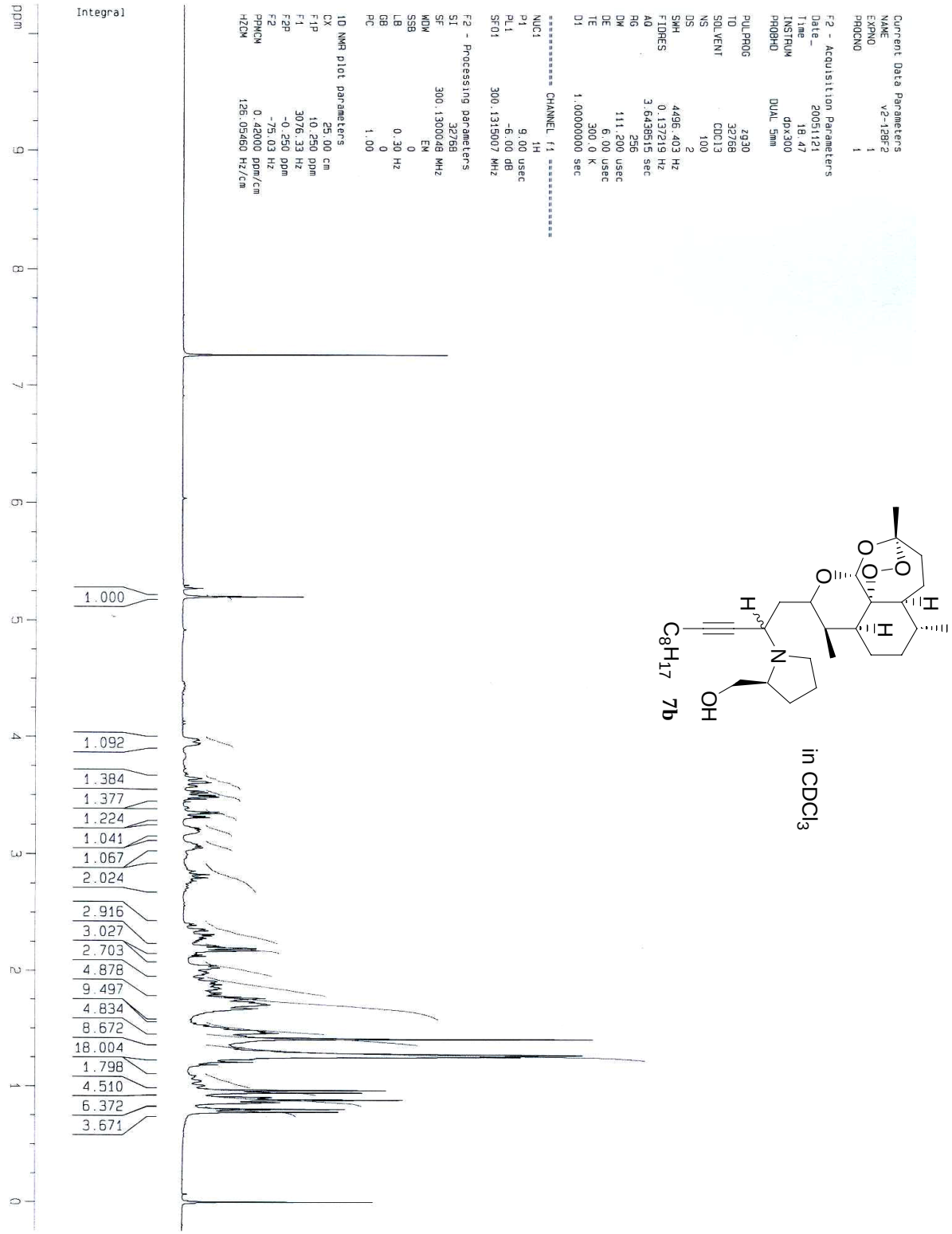
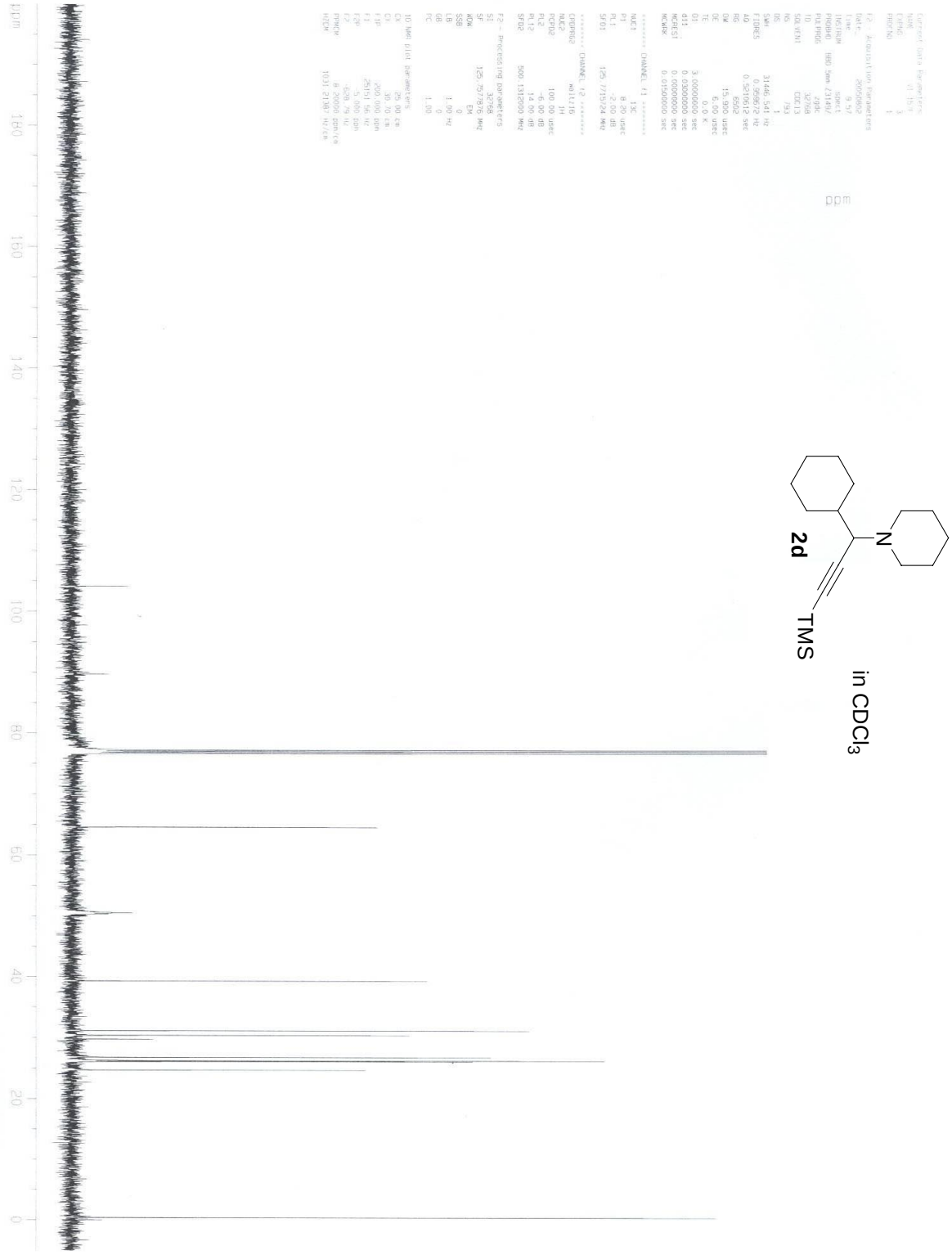
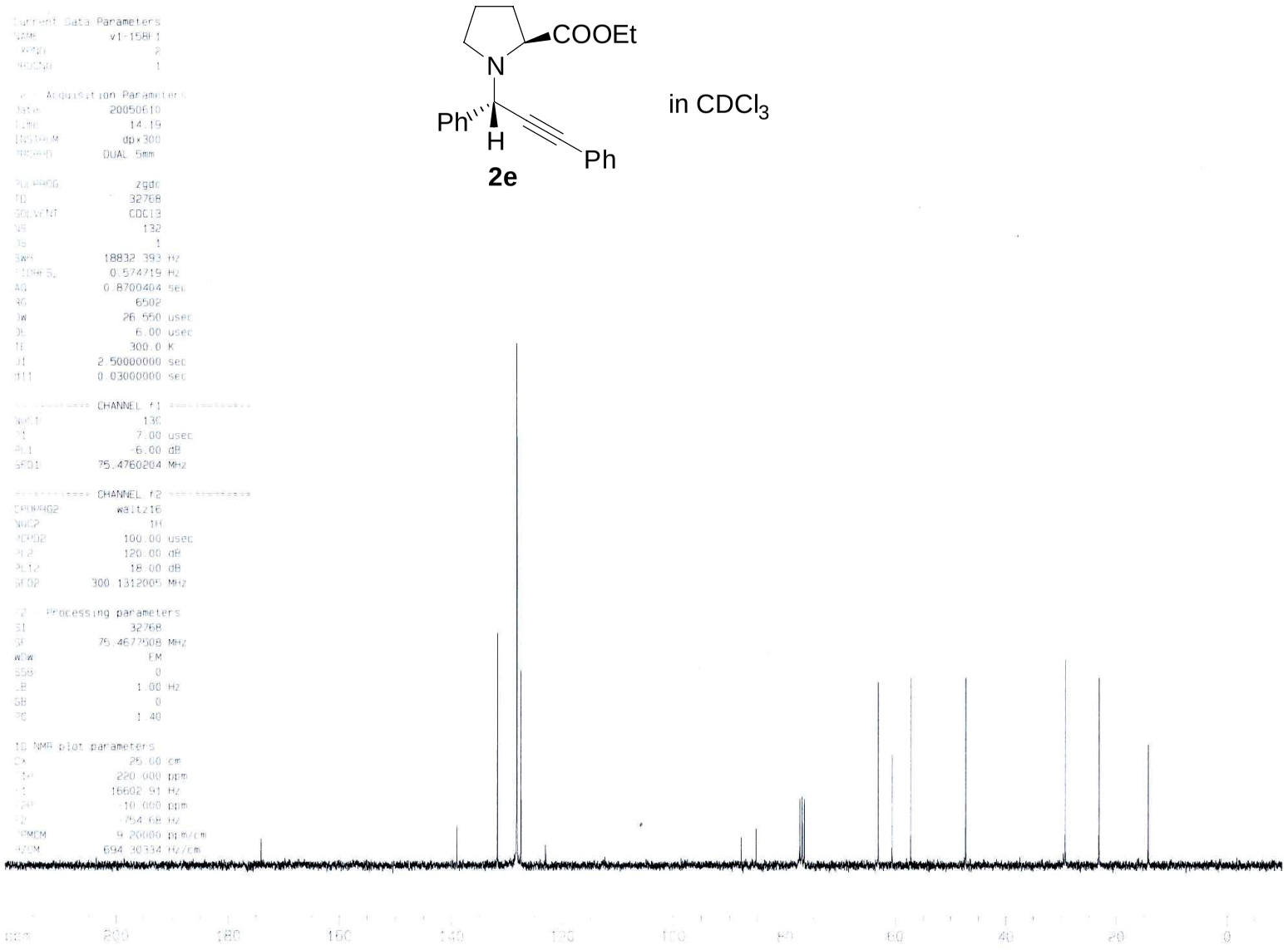
2.0628
1.0171
1.0307
2.1147
3.0087
7.5745
3.4224
2.3315
0.9404
2.1195
1.0076
3.2837
3.0767
Ph
6a
OH
in CDCl3


Integral
2.359
3.515
1.000
1.023
1.527
1.157
2.182
1.336
1.268
2.763
2.163
20.411
3.203
4.671
8.318
3.915
3.894
Ph
6b
OH
in CDCl3


Integral
1.000
1.001
2.075
1.032
1.101
2.140
2.400
2.205
1.418
10.898
4.727
7.349
11.506
1.244
3.558
3.726
3.395
ppm
0
1
2
3
4
5
6
7
8
9
Current Data Parameters
NAME v2-29f1
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20050805
Time_ 15.11
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 64
DS 0
SWH 8012.820 Hz
FIDRES 0.244532 Hz
AQ 2.0447731 sec
RG 228.1
DW 62.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 13.20 usec
PL1 -4.00 dB
SFO1 400.1324008 MHz
F2 - Processing parameters
SI 32768
SF 400.1300066 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 25.00 cm
CY 8.14 cm
F1P 10.250 ppm
F1 4101.33 Hz
F2P -0.250 ppm
F2 -100.03 Hz
PPMCM 0.42000 ppm/cm
HZCM 168.05460 Hz/cm
O
O
O
O
H
H
H
N
OH
C8H17
7a
in CDCl3

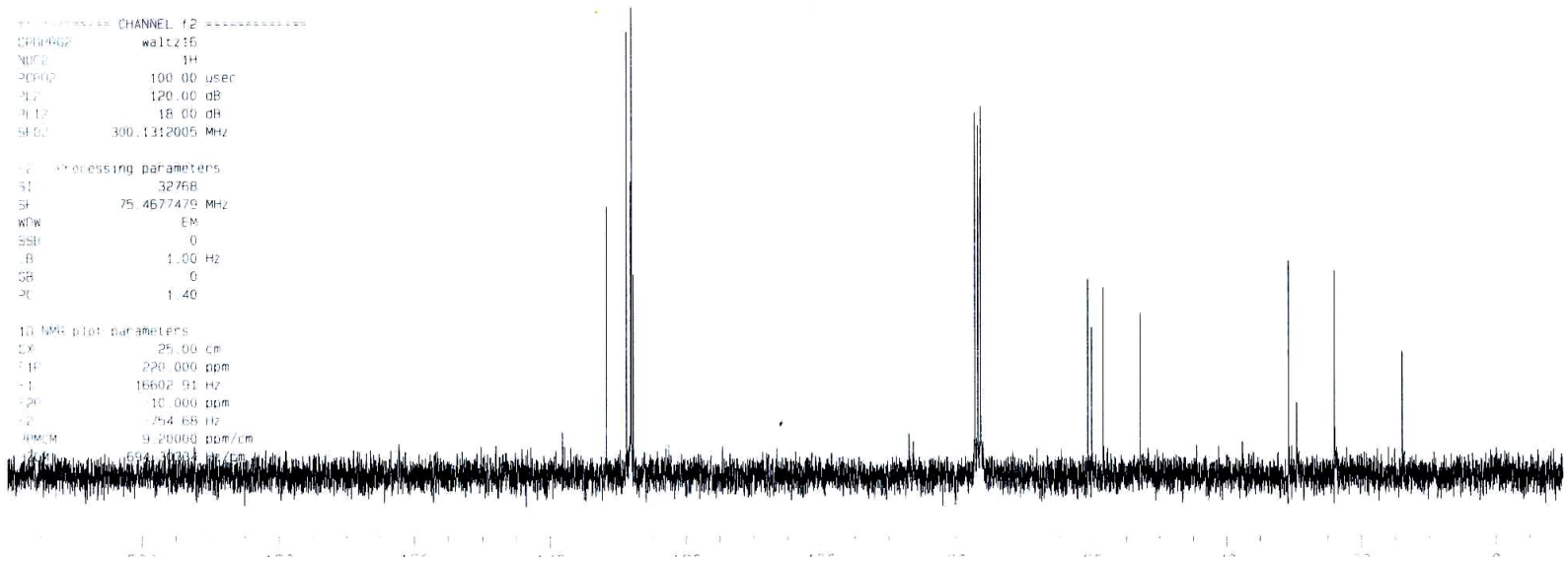

Current Data Parameters
NAME v2-128F2
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20051121
Time 18.47
INSTRUM dpx300
PROBHD DUAL 5mm
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 100
DS 2
SWH 4496.403 Hz
FIDRES 0.137219 Hz
AQ 3.643851S sec
RG 256
DW 111.200 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 9.00 usec
PL1 -6.00 dB
SFO1 300.1315007 MHz
F2 - Processing parameters
SI 32768
SF 300.1300048 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 25.00 cm
F1P 10.250 ppm
F1 3076.33 Hz
F2P -0.250 ppm
F2 -75.03 Hz
PPMCM 0.42000 ppm/cm
HZCM 126.05460 Hz/cm
Integral
1.000
1.092
1.384
1.377
1.224
1.041
1.067
2.024
2.916
3.027
2.703
4.878
9.497
4.834
8.672
18.004
1.798
4.510
6.372
3.671
ppm
9
8
7
6
5
4
3
2
1
0
H
O
O
O
O
H
H
N
OH
C8H17 7b
in CDCl3

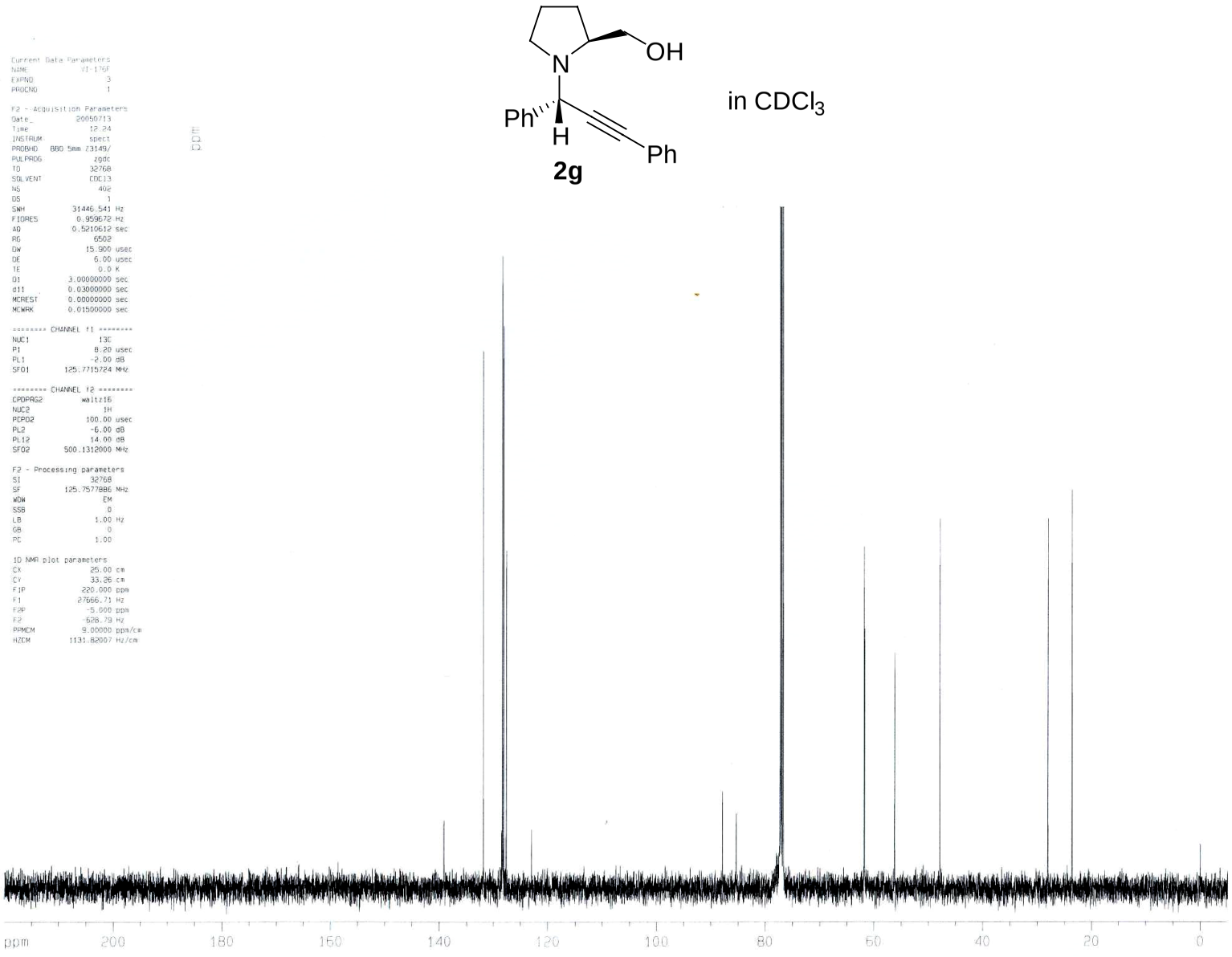

N
TMS
2d
in CDCl3

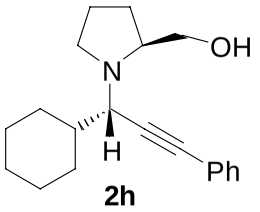

Current Data Parameters
NAME v1-158f1
EXPNO 2
PROCNO 1
1H Acquisition Parameters
Date_ 20050610
Time 14.19
INSTRUM dpx300
PROBHD DUAL 5mm
PULPROG zgdc
TD 32768
SOLVENT CDCl3
NS 132
DS 1
SWH 18832.393 Hz
FIDRES 0.574719 Hz
AQ 0.8700404 sec
RG 6502
DW 26.550 usec
DE 6.00 usec
TE 300.0 K
D1 2.50000000 sec
D11 0.03000000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 7.00 usec
PL1 -6.00 dB
SFO1 75.4760204 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 120.00 dB
PL12 18.00 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677508 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 25.00 cm
F1P 220.000 ppm
F1 16602.91 Hz
F2P -10.000 ppm
F2 -754.68 Hz
PPMCM 9.20000 ppm/cm
HZCM 694.30334 Hz/cm
COOEt
N
Ph
H
Ph
2e
in CDCl3
ppm
200
180
160
140
120
100
80
60
40
20
0

2e'

in $CDCl_3$



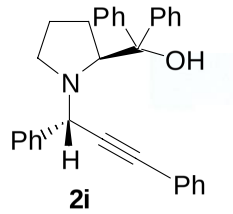

Current Data Parameters
NAME VI-175F
EXPNO 3
PROCNO 1
F2 - Acquisition Parameters
Date_ 20050713
Time 12.24
INSTRUM spect
PROBHD BBO 5mm Z3149/
PULPROG zgdc
TD 32768
SOLVENT CDCl3
NS 402
DS 1
SWH 31446.541 Hz
FIDRES 0.959672 Hz
AQ 0.5210612 sec
RG 6502
DW 15.900 usec
DE 6.00 usec
TE 0.0 K
D1 3.00000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 8.20 usec
PL1 -2.00 dB
SF01 125.7715724 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -6.00 dB
PL12 14.00 dB
SF02 500.1312000 MHz
F2 - Processing parameters
SI 32768
SF 125.7577886 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 25.00 cm
CY 33.26 cm
F1P 220.000 ppm
F1 27666.71 Hz
F2P -5.000 ppm
F2 -628.79 Hz
PPMCM 9.00000 ppm/cm
HZCM 1131.82007 Hz/cm
EDITE
N
OH
Ph
H
Ph
2g
in CDCl3
ppm
200
180
160
140
120
100
80
60
40
20
0


OH
N
H
Ph

2h

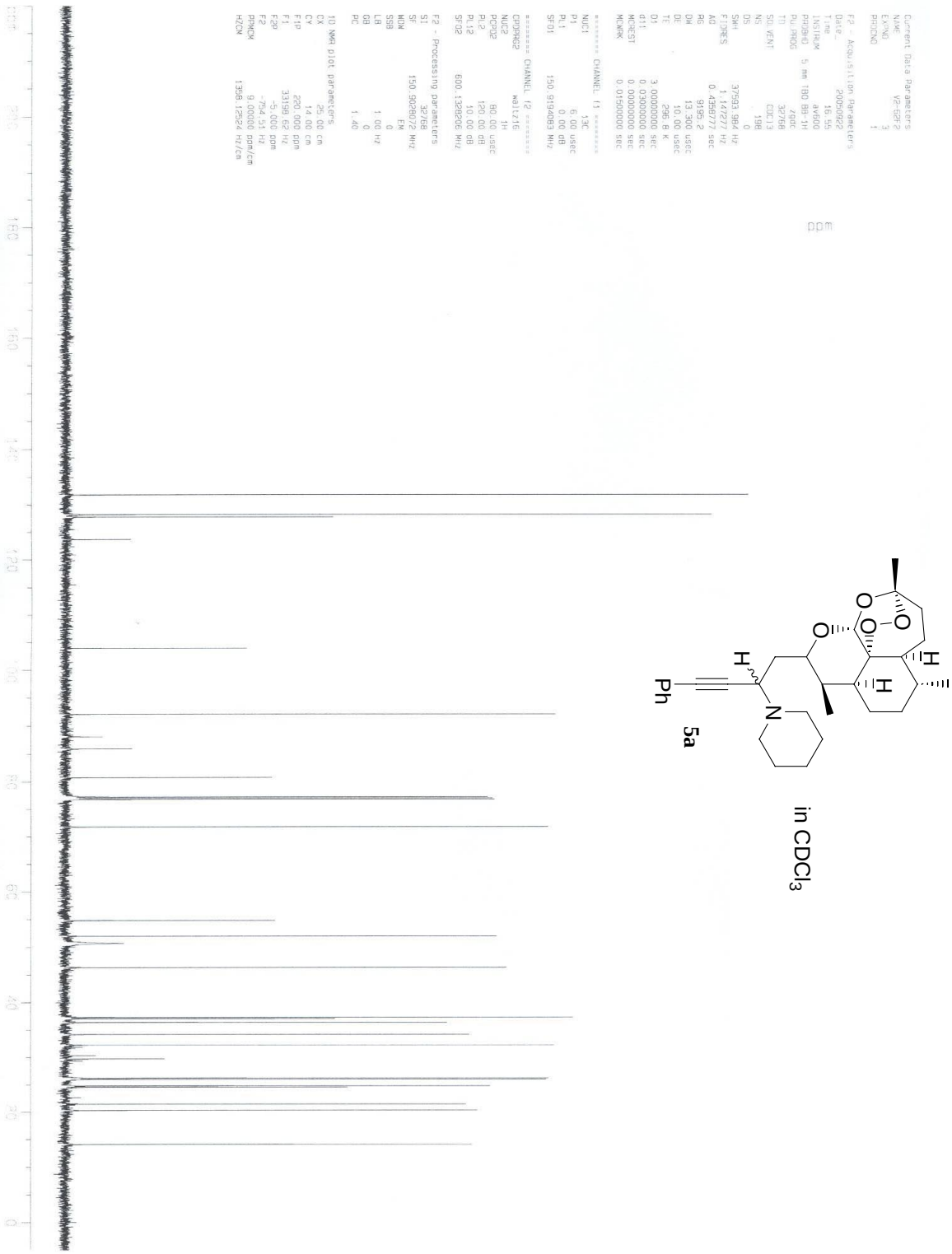
in $CDCl_3$

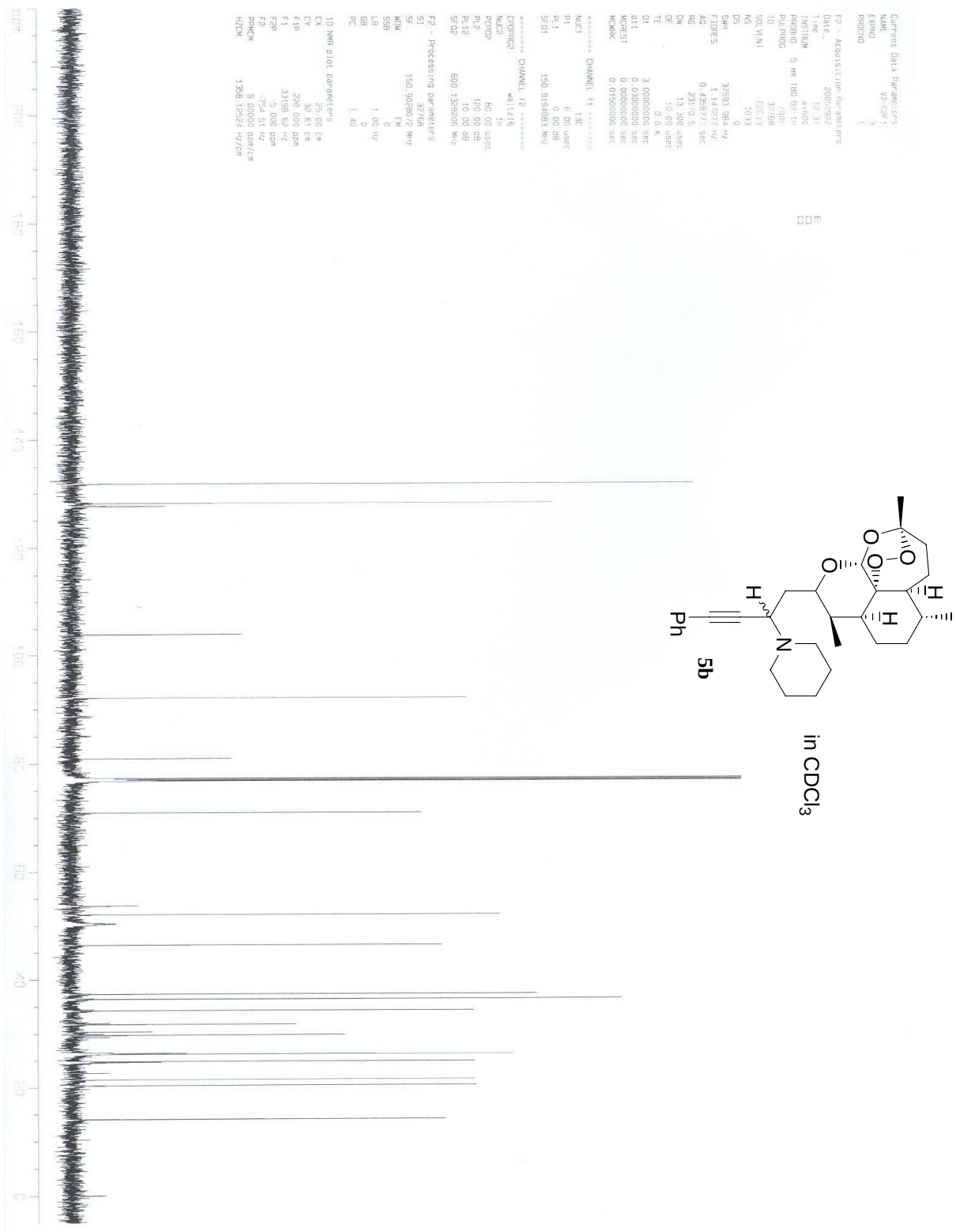
Current Data Parameters
NAME v2_36F
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20050827
Type 1D_13
INSTRUM spect
PROBHD Dual 5mm
PULPROG zgdc
TD 32768
SOLVENT CDCl3
NS 376
DS 1
SWH 18832.393 Hz
FIDRES 0.574719 Hz
AQ 0.8700404 sec
RG 6502
DW 26.550 usec
DE 6.00 usec
TE 300.0 K
D1 2.50000000 sec
D11 0.03000000 sec
CHANNEL f1
NUC1 13C
P1 7.00 usec
PL1 6.00 dB
SFO1 75.4760204 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 120.00 dB
PL12 18.00 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677474 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 25.00 cm
F1P 220.000 ppm
F1 16602.91 Hz
F2P 10.000 ppm
F2 754.68 Hz
PPMCM 9.20000 ppm/cm
HZCM 694.82532 Hz
200
180
160
140
120
100
80
60
40
20
0

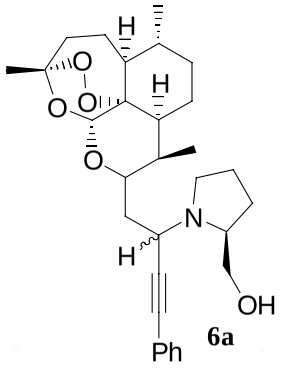


2i

in $CDCl_3$


Ph
5a
in $CDCl_3$

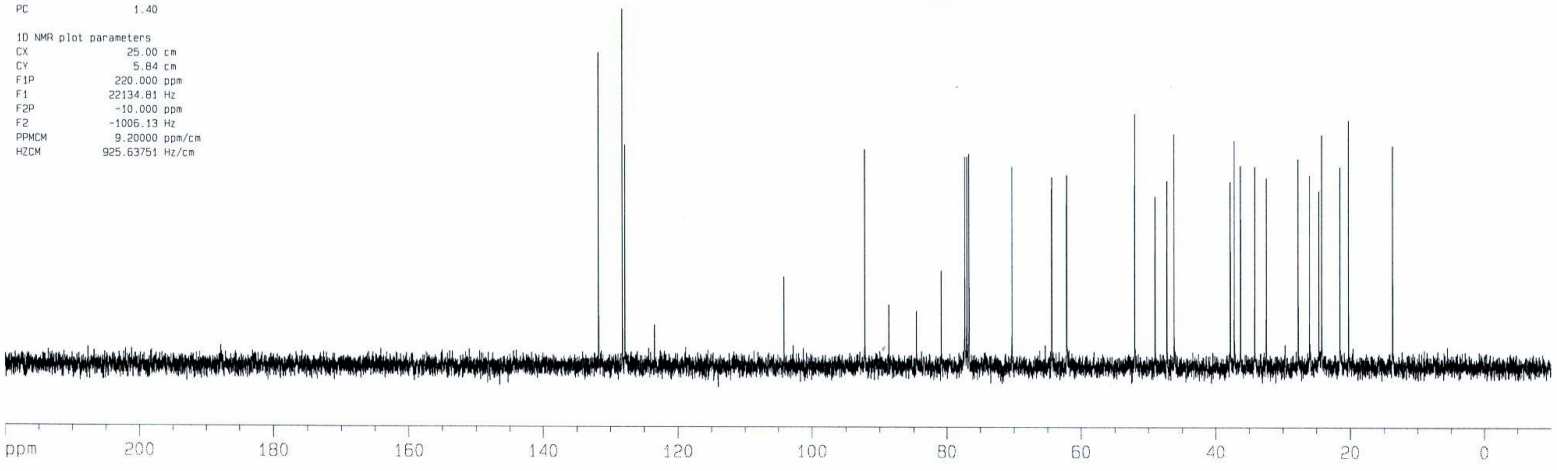

Ph
5b
in $CDCl_3$

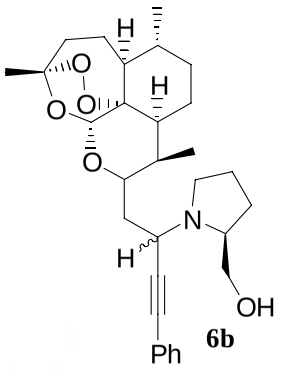


6a

in $CDCl_3$

```
Current Data Parameters
NAME                 v2-25F1
EXPNO                      2
PROCNO                     1

F2 - Acquisition Parameters
Date_               20050805
Time                   18.27
INSTRUM                av400
PROBHD   5 mm QNP 1H/13
PULPROG                zgdc
TD                     32768
SOLVENT                CDCl3
NS                       153
DS                         0
SWH               26178.010 Hz
FIDRES                0.798889 Hz
AQ                    0.6259188 sec
RG                     1290.2
DW                    19.100 usec
DE                     6.00 usec
TE                     300.0 K
D1                2.50000000 sec
d11               0.03000000 sec

======== CHANNEL f1 ========
NUC1                      13C
P1                       9.80 usec
PL1                     -5.00 dB
SFO1             100.6238364 MHz

======== CHANNEL f2 ========
CPDPRG2               waltz16
NUC2                       1H
PCPD2                   80.00 usec
PL2                     -4.00 dB
PL12                     8.00 dB
SFO2             400.1320007 MHz

F2 - Processing parameters
SI                         32768
SF               100.6127700 MHz
WDW                           EM
SSB                            0
LB                        1.00 Hz
GB                             0
PC                          1.40

1D NMR plot parameters
CX                        25.00 cm
CY                         5.84 cm
F1P                     220.000 ppm
F1                    22134.81 Hz
F2P                     -10.000 ppm
F2                    -1006.13 Hz
PPMCM                  9.20000 ppm/cm
HZCM                 925.63751 Hz/cm
```

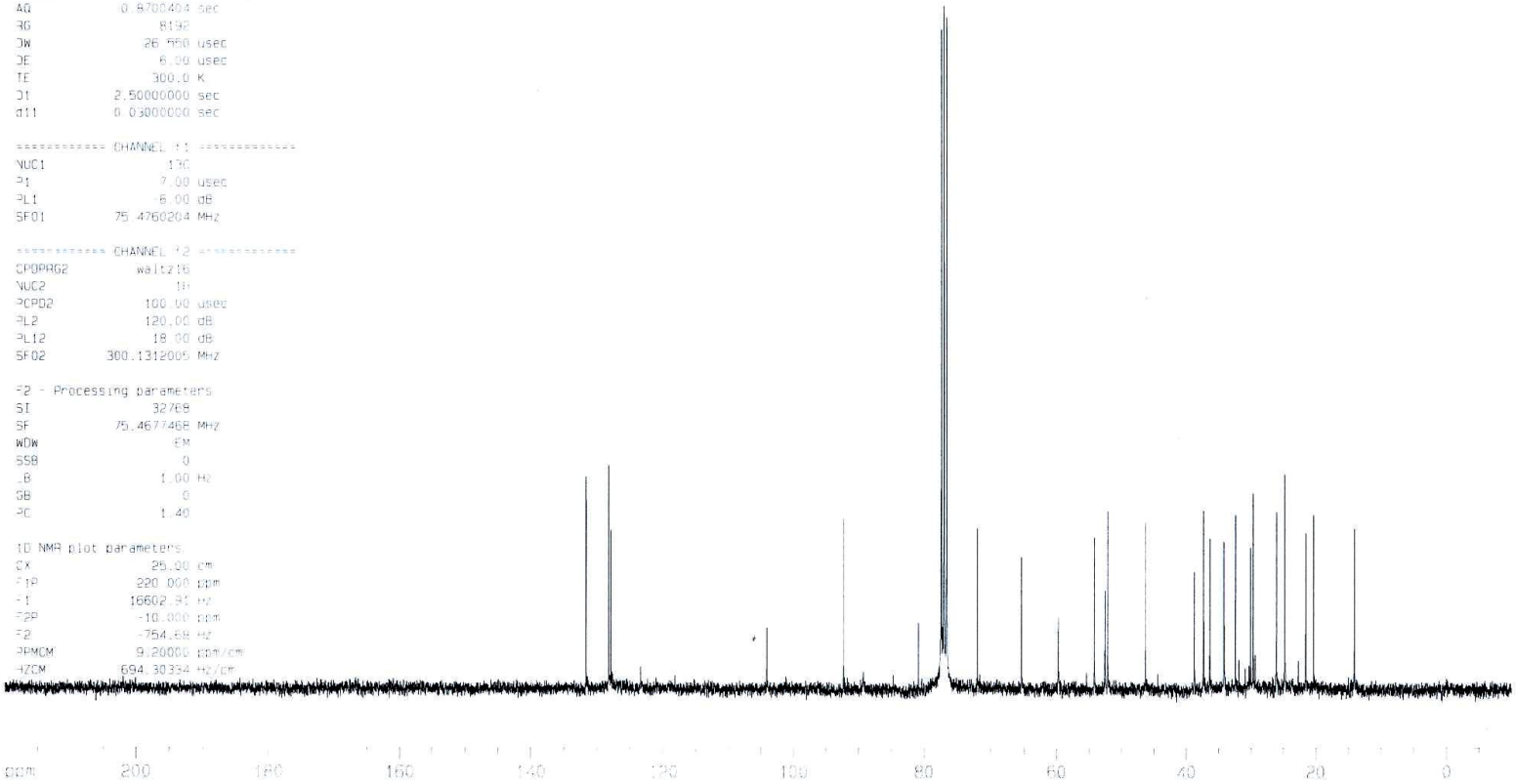


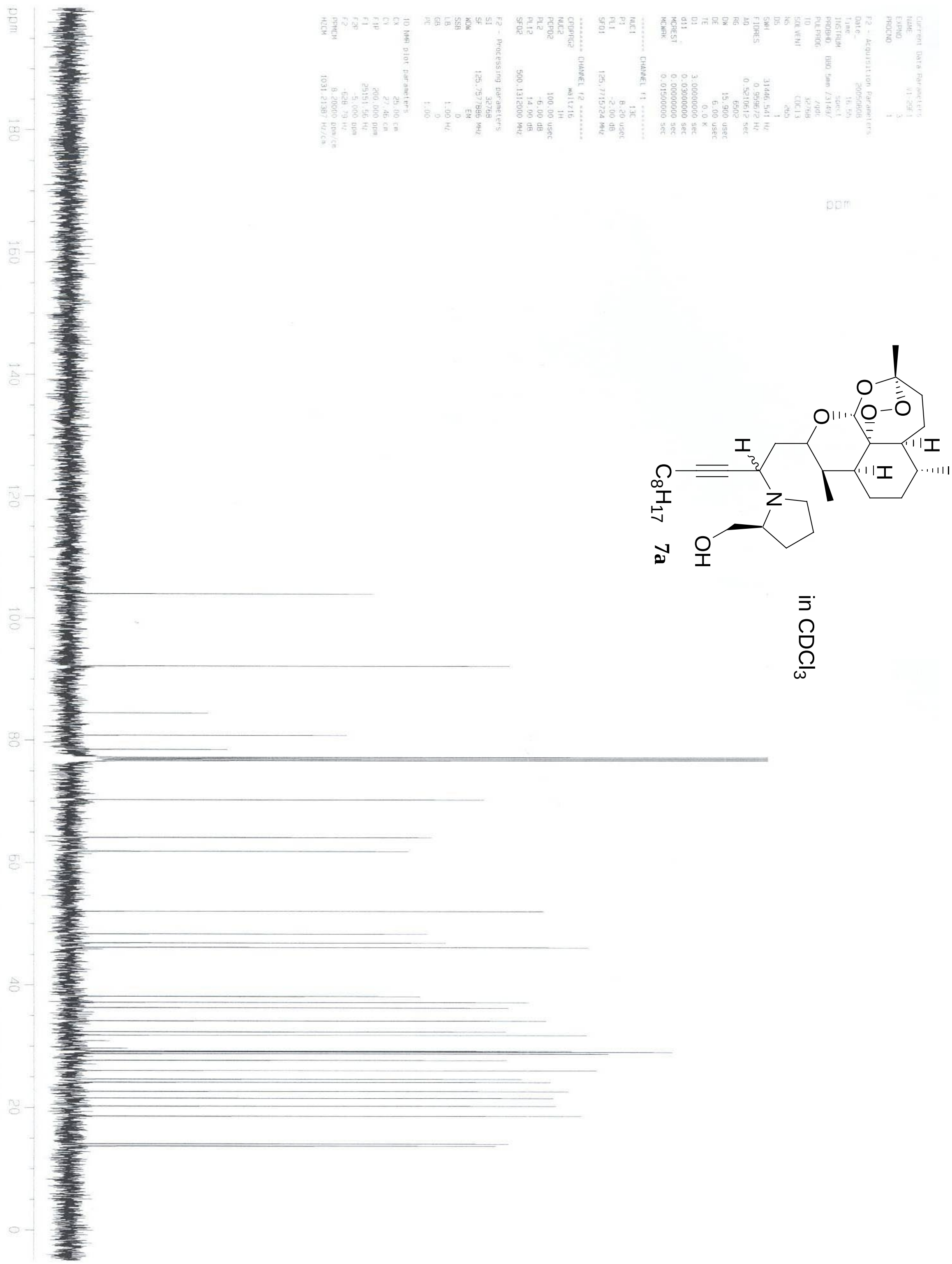


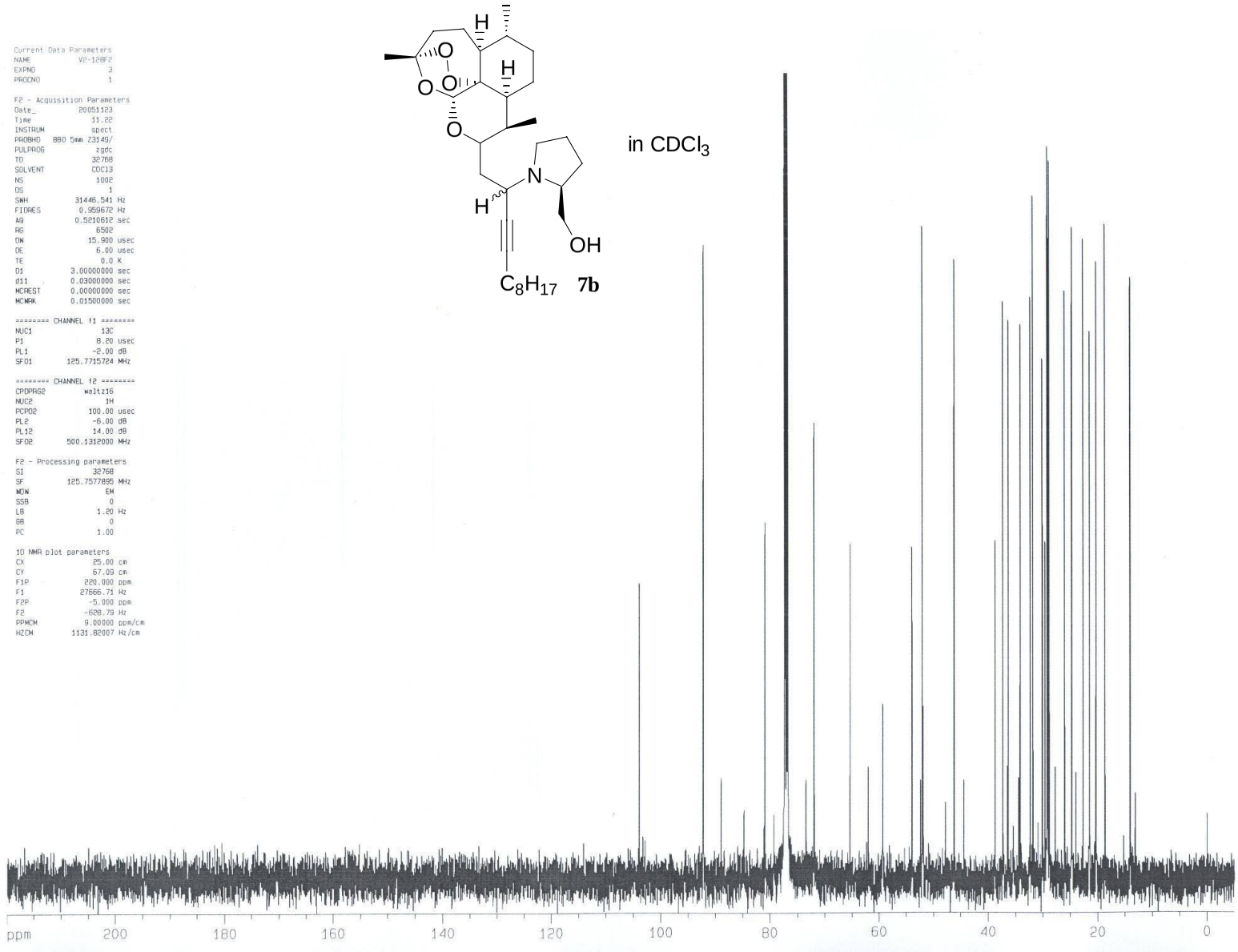
6b

in $CDCl_3$

```
Current Data Parameters
NAME                  v2-7B12
EXPNO                       2
PROCNO                      1

F2 - Acquisition Parameters
Date_              20051001
Time                    2.39
INSTRUM                dpx300
PROBHD          DUAL 5mm

PULPROG                 zgdc
TD                     32768
SOLVENT                CDCl3
NS                      9151
DS                         1
SWH                18832.393 Hz
FIDRES              0.574719 Hz
AQ                  0.8700404 sec
RG                       8192
DW                    26.550 usec
DE                     6.00 usec
TE                     300.0 K
D1                 2.50000000 sec
d11                0.03000000 sec

========== CHANNEL f1 ==========
NUC1                      13C
P1                       7.00 usec
PL1                      6.00 dB
SFO1               75.4760204 MHz

========== CHANNEL f2 ==========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                  100.00 usec
PL2                    120.00 dB
PL12                    18.00 dB
SFO2              300.1312005 MHz

F2 - Processing parameters
SI                       32768
SF                 75.4677468 MHz
WDW                         EM
SSB                          0
LB                        1.00 Hz
GB                           0
PC                        1.40

1D NMR plot parameters
CX                      25.00 cm
F1P                   220.000 ppm
F1                  16602.31 Hz
F2P                   -10.000 ppm
F2                   -754.68 Hz
PPMCM                 9.20000 ppm/cm
HZCM                694.30334 Hz/cm
```




ppm
180
160
140
120
100
80
60
40
20
0
7a
in $CDCl_3$


Current Data Parameters
NAME V2-128F2
EXPNO 3
PROCNO 1
F2 - Acquisition Parameters
Date_ 20051123
Time 11.22
INSTRUM spect
PROBHD 880 5mm Z3149/
PULPROG zgdc
TD 32768
SOLVENT CDCl3
NS 1002
DS 1
SWH 31446.541 Hz
FIDRES 0.959672 Hz
AQ 0.5210612 sec
RG 6502
DW 15.900 usec
DE 6.00 usec
TE 0.0 K
D1 3.00000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 8.20 usec
PL1 -2.00 dB
SF01 125.7715724 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -6.00 dB
PL12 14.00 dB
SF02 500.1312000 MHz
F2 - Processing parameters
SI 32768
SF 125.7577895 MHz
WDW EM
SSB 0
LB 1.20 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 25.00 cm
CY 67.09 cm
F1P 220.000 ppm
F1 27666.71 Hz
F2P -5.000 ppm
F2 -628.79 Hz
PPMCM 9.00000 ppm/cm
HZCM 1131.82007 Hz/cm
H
O
O
O
O
H
N
H
OH
C8H17
7b
in CDCl3
ppm
200
180
160
140
120
100
80
60
40
20
0